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Chemical & Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere-Year Ending June 30, 1973

Battelle Columbus Labs.

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The scope of the project work covers the generation of automobile particulate matter with specially chosen, measured engines. A major experimental study has been necessary to develop test procedures which give as true as possible values of the particulate emissions. The gaseous measurements enabled a detailed assessment of vehicle operation to be made.

Electron microscope studies of the exhaust particles suggest four possible mechanisms of particle growth; agglomeration, condensation, crystal growth, deposition and ablation of exhaust system deposits.

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CHEMICAL AND PHYSICAL CHARACTERIZATION OF AUTOMOTIVE EXHAUST PARTICULATE MATTER IN THE ATMOSPHERE (Year ending June 30, 1973)

by

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MANAGEMENT SUMMARY

The purpose of the program is to determine the physical and chemical characteristics of exhaust particulate matter from internal combustion engines as a function of sampling procedure, engine operating conditions (including emission control systems), fuel composition, and residence time in the atmosphere. Emphasis will be placed on predicting the fate of exhaust particulate matter in the atmosphere.

The scope of the project work covers the generation of automobile particulate matter with specially chosen, measured engines. The auto exhaust is diluted in two stages: first in a mixing tunnel, then in a large residence chamber with relatively small wall loss. The properties of exhaust particles are being studied from their initial formation to their ultimate removal from the chamber atmosphere.

A major experimental study has been necessary to develop test procedures which give as true as possible values of the particulate emissions. This has been a consequence of the very small weights of the particulate matter and the very large dilutions necessary to simulate the way they exist in the atmosphere, as well as the fact that the collection of particulate material is strongly affected by the techniques used to collect them. Thus the geometry, temperature, and velocity of the sample stream had to be set to optimums, as well as the size, weight, and type of filter used, weighing techniques, and the many car operating variables.

In the study thus far, two identical 1970 Fords with matched standard 1971 engines (engine modification emission controls) were conditioned similarly for 5,000 miles on unleaded fuel, and shown to have equivalent emission characteristics. The vehicles then were operated for an additional 8,000 miles, one on unleaded fuel, the other on the same base fuel to which had been added 2.5 grams lead per gallon measured as TEL Motor Mix. During this phase, exhaust gas emissions and particulate matter were measured at preselected intervals. The gaseous measurements enabled a detailed assessment of vehicle operation to be made. The particulate matter was sampled from the dilution tunnel and the residence chamber in each run. The material collected from the dilution tunnel is considered representative for fresh auto exhaust as it is emitted into the atmosphere. The particles sampled from the residence chamber inidcate the nature of the air-suspended fraction after aging for periods up to 24 hours.

In this contract year two major problem areas were encountered and significant efforts were devoted to solving them. The

first relates to reproducible day-to-day operation of vehicles for particle generation. Vehicle operation during the cold start portion of the cycle and the operation of the choke were found to be critical. These problems have been identified and the procedures have been standardized for reproducibility.

The second problem relates to the measurement by filtration of the carbonaceous particulate matter in vehicle exhaust. A filter sampling system and filter media have been selected that show reproducible weight gain. Work on the filtration problem continues with the aim of establishing a procedure for absolute measurements.

The total particulate emission rate from the nonleaded car is in the range 0.04-0.075 gram per mile for the 1972 FTP (Federal Test Procedures) Cycle. There is a correlation between the particulate and the hydrocarbon emission rates. The particulate emissions from leaded fuel were 0.05 to 0.15 g/mile more than those from unleaded fuel, or from 60 to 100 percent higher when compared at the same hydrocarbon emission level. For both fuels the mass median equivalent diameter of the exhaust particles suspended in the dilution tunnel and in the residence chamber were in the submicron size range. Measurements with the Minnesota Aerosol-Analyzing System indicate a bimodal size distribution.

Electron microscope studies of the exhaust particles suggest four possible mechanisms of particle growth; agglomeration, condensation, crystal growth, deposition and ablation of exhaust system deposits.

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FOURTH ANNUAL SUMMARY REPORT

on

CHEMICAL AND PHYSICAL CHARACTERIZATION OF
AUTOMOTIVE EXHAUST PARTICULATE MATTER
IN THE ATMOSPHERE

to

COORDINATING RESEARCH COUNCIL
(CRC-APRAC PROJECT NO. CAPE-19-70)

and

ENVIRONMENTAL PROTECTION AGENCY
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from

BATTELLE
Columbus Laboratories

July 25, 1974

INTRODUCTION

This report describes a fourth year[1,2,3] of studies directed toward determining the fate of auto exhaust particles in the atmosphere. During this year two preconditioned cars have been operated on test cycles under controlled conditions to generate particulate matter for detailed

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(1) C. W. Melton, et al, "Physical-Chemical Characteristics of Particles Associated with Polynuclear Aromatic Hydrocarbons Present in Automobile Exhaust", Final Summary Technical Report for the period January 24, 1969, to March 31, 1970, to Coordinating Research Council (APRAC-CAPE-12-68-Neg. 59), January 29, 1970.

(2) J. F. Foster, et al, "Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere", Final Summary Report for the period July 1, 1970, to June 24, 1971, to Coordinating Research Council (CAPE-12-68-Neg. 59 and CAPE-19-70), October 6, 1972.

(3) C. W. Melton, R. I. Mitchell, D. A. Trayser, J. F. Foster, "Chemical and Physical Characterization of Automotive Exhaust Particulate Matter in the Atmosphere", Final Summary Report for the period June 25, 1971, to June 30, 1972, to Coordinating Research Council (CAPE-19-70) and Environmental Protection Agency (Contract No. 68-02-0205), June 14, 1973.

study. In this report are presented descriptions of the apparatus, including cars, exhaust-dilution tunnel, residence chamber for aging particulate matter in suspension, and instrumentation; and procedures, including preparation and maintenance of the cars, test cycles, and measurements of the properties of generated particulate matter. Development and standardization of apparatus and procedures was carried out during the early part of the year by operation of the cars, as well as by tests on individual segments of the associated apparatus.

Subsequently a total of 58 runs was completed in the integrated test system in which particles were generated from both leaded and unleaded fuels. Results from the 58 tests are tabulated in the experimental section.

OBJECTIVE

The objective of the program is to determine the physical and chemical characteristics of exhaust particulate matter from internal-combustion engines as a function of sampling procedure, engine operating conditions, lead content of the fuel, and the length of residence in the atmosphere under various conditions.

EXPERIMENTAL APPARATUS AND PROCEDURES

In this project, automobile exhaust particulates are generated from leaded or unleaded fuels used separately in each of two otherwise identical automobiles having specially chosen, measured engines selected for similarity. The auto exhaust is diluted and mixed with air passing through a 36-foot-long tube (the "dilution tunnel"), then passed into a 2100-cubic-foot residence chamber large enough to minimize wall losses. Figure 1 is a perspective view of the test apparatus with the test car positioned on the chassis dynamometer. Exhaust is directed into the dilution tunnel, from which a portion is taken into the residence chamber.

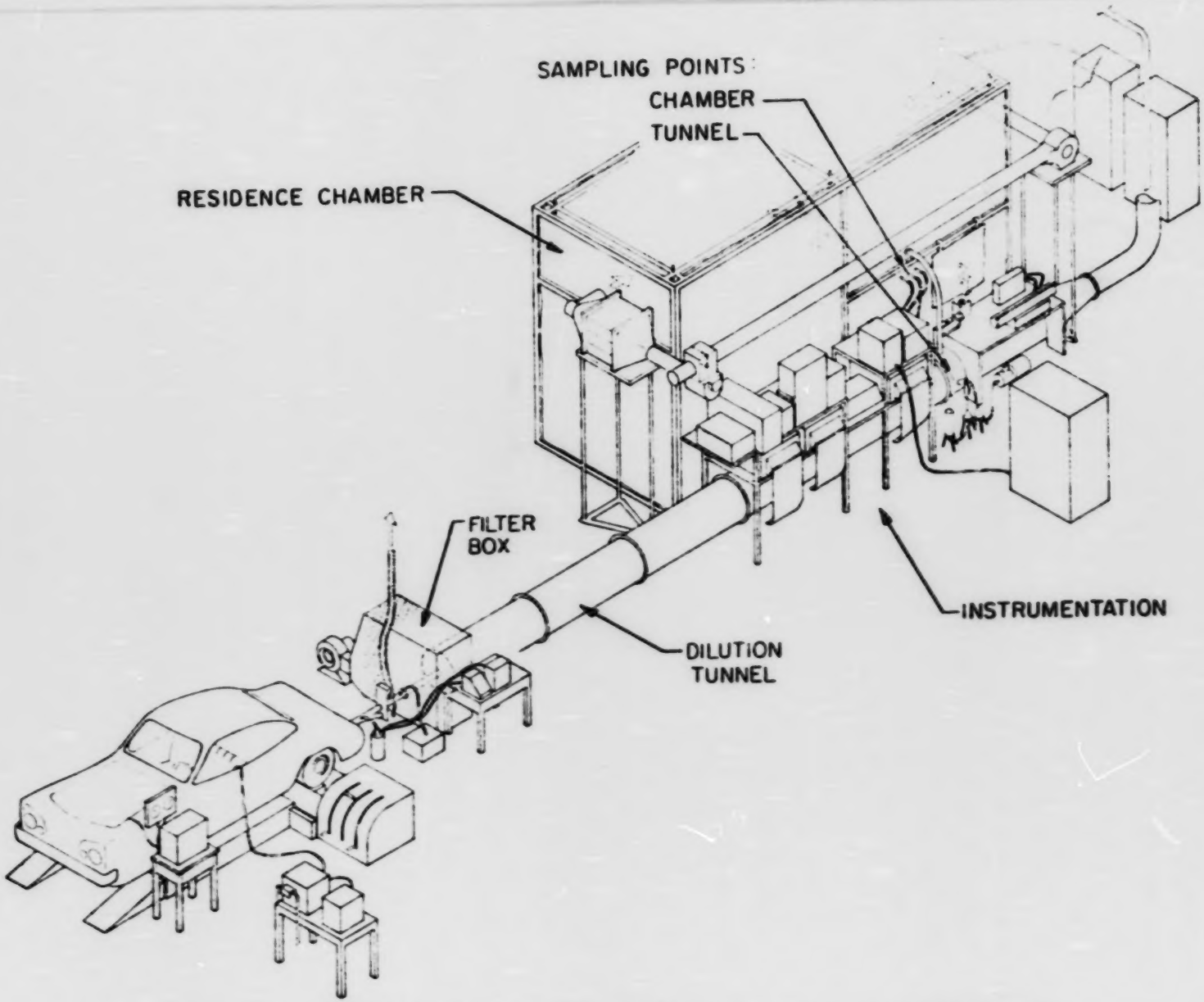

FIGURE 1. PERSPECTIVE VIEW OF TEST APPARATUS AND AUXILIARY INSTRUMENTATION

Fuels

Two fuels were purchased from Mobil Research and Development Corporation in January, 1972. These gasolines were identical except for lead content. Fuel RE-141B was unleaded and RE-141C had 2.49 g Pb/gal. Measured characteristics of the two fuels are reported in the Appendix, Table A-1, pages A-1 to A-3.

Project Cars

Two 1970 Fairlane Fords with 1971 engines were prepared last year for exhaust-gas generation. The engines were 351 CID V-8's with 2-barrel carburetors and automatic transmissions. In order to make the two automobiles closely comparable, specially matched and measured 1971 engines were made available by the Ford Motor Company and were installed in the two vehicles by project personnel at Battelle. There is no significant difference between the two cars, although one is color coded white (Car W) and the other blue (Car B) for identification. Only unleaded fuel has been used in the white car. Only leaded fuel has been used in the blue car, following a 4000-mile conditioning on unleaded fuel.

Conditioning of Cars

Each car was operated 8,000 miles to stabilize deposits. Beginning at 0 miles, each car was driven on a chassis dynamometer for 4000 miles with unleaded fuel, using a (modified) Durability Driving Schedule[1]. Periodic measurements of volatile emissions were made during the 4000 miles to compare emission characteristics. Car W continued for another 4000 miles on the modified Durability Driving Schedule with RE-141B unleaded fuel, but Car B was operated for the second 4000 miles on leaded fuel RE-141C.

---

(1) Standard Durability Driving Schedule as described in the Federal Register, Volume 35, No. 136, Part II, July 15, 1970, without the 70 mph lap.

Test Cycles

A modified Standard Urban Driving Cycle[1] was used during most of the test runs, in which 35 seconds was added to the standard 20 seconds of idle after engine start to give a total of 55 seconds idle time before the first acceleration mode. This cycle is designated the "modified LA-4" cycle.

In some test runs the standard cycle, with the specified initial 20-second idle, was used. This cycle is designated as the "LA-4" cycle.

Test Run Procedure

In cooperation with the CAPE-19 Project Group the following preconditioning and particulate-emissions test procedure was established:

Preconditioning

- 100 miles on modified[2] MVMA Durability Schedule
- Two modified[3] EPA (LA-4) Urban Driving Cycles immediately after the 100-mile durability run
- Record tailpipe CO during EPA cycles
- Check tailpipe CO at idle and adjust, if necessary, to 1.0 ± 0.2 percent.
- Record tailpipe CO and O_2 at idle and 50 mph cruise before shutdown for overnight soak
- Overnight soak period of at least 16 hours at 70 F ± 2 F.

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(1) Federal Register, Volume 35, No. 136, Part II, July 15, 1970.

(2) Standard Durability Driving Schedule as described in the Federal Register, Volume 35, No. 136, Part II, July 15, 1970, without the 70 mph lap.

(3) Standard Urban Driving Cycle as described in July 15, 1970 Federal Register modified as described in Test Cycles above (basically 35 seconds additional time at idle before first acceleration mode).

Test Run

- Actuate throttle, set choke to closed, adjust choke drive system to starting position
- Simultaneously start particulate-filter sample pump, open sample-pipe valve to chamber, start tunnel-bag sampling
- After 15 seconds start car
- 15 seconds after engine start "kick down" off high idle
- 25 seconds after engine start put car in gear
- 35 seconds after engine start, start speed controller tape (first acceleration mode begins 20 seconds later)
- 5 seconds after full stop at end of last mode of cycle close sample-pipe valve and stop tunnel-bag and particulate sampling pumps.

Post-Cycle Operation Check

- Operate car at idle, 35 mph cruise, and 50 mph cruise.
- Record tailpipe CO (Runs 12-1 to 1-15, Appendix, Table A-4) for evidence of change since preconditioning, and for check on emissions plus calculation of air/fuel ratio. Supporting data on tailpipe oxygen, and on CO_2 and HC in diluted exhaust of tunnel were found to be less reliable for emissions and air/fuel ratio determinations, so improved instrumentation was employed in the next experimental phase.
- Record tailpipe CO, CO_2, O_2, and HC for operation check, emissions, and air/fuel ratio. (Runs 4-4 to 5-22, Table A-4)
- Shut off engine.

Engine Air Flow Measurements

A laminar flow meter and a differential pressure transducer were installed on the unleaded-fuel white car prior to the regular test runs to measure engine air flow during both the LA-4 cycles and steady cruise operation under the above operating procedures.

With the laminar flow meter connected to the engine air cleaner inlet, it was not feasible to preheat the carburetor air as in the normal configuration. Consequently, carburetor inlet air temperatures were slightly lower during the air flow measurement runs than during regular test runs. The effect of this departure from normal engine air flow is negligible.

One run was made to measure engine air flow during a cold-start LA-4 cycle, and another run to measure engine air flow during a hot-start LA-4 cycle. The average flow rate during the cold-start run was 28.2 scfm, and during the hot-start run was 27.2 scfm. These carburetor air rates are converted to exhaust-gas flow rates, including water vapor, by multiplying by a factor of 1.07. Thus, the average exhaust gas flow during the cold-start modified LA-4 driving cycle was 28.2 x 1.07 = 30.2 scfm. This value represents a tunnel dilution ratio of 30 for a tunnel flow of 905 cfm. Measured variations of engine air flow with road speed and of air-fuel ratio with engine air flow are given in the Appendix, pages A-4 to A-6.

Choke Operation

It was necessary to repeat for each run in a series the same choke opening schedule because it was found that choke operation influenced strongly the particle emissions. In addition, slower choke opening than would normally occur at laboratory ambient temperature was needed in conjunction with the programmed throttle controller to reduce the chance of stumble and stall in the first minute or so, which occurred with the regular vehicle choke. However, decreasing the rate at which the choke opens increased exhaust emissions, and the extent to which the choke schedule could be modified was limited by the maximum acceptable HC and CO composite (tunnel-bag) emissions from the cycle. The tunnel-bag emissions considered acceptable for the 1971 project cars on the LA-4 driving schedule were: 4.6 g/mile HC, 47.0 g/mile CO, and 3 g/mile NO. The small amounts of particulate matter generated in the single modified or standard LA-4 cycle required that these limits be approached closely in order to collect weighable amounts. Four different choke schedules were used in the course of the experimental program to accommodate operating requirements and other limitations. Details of the experimental development of acceptable choke operation are given in the Appendix, pages A-10 to A-17.

Dilution Tunnel

A dilution tunnel simulates the real environment by inducing rapid dilution of the exhaust as it issues from the tailpipe. Mixing with constant proportions of filtered atmospheric air under reproducible experimental conditions permits accurate sampling of the dilute mixture (usually diluted 30:1). The dilution tunnel used in these studies was constructed according to the design developed at the Du Pont Petroleum Laboratory[1]. The dilution tunnel residence chamber, and sampling apparatus are shown in Figure 1, page 3. Details of configuration, operation, and arrangement of auxiliary apparatus are given in the Appendix, pages A-18 to A-32.

Residence Chamber

A rectangular residence chamber with flexible walls of black polyethylene sheeting on a supporting frame was used to contain a composite sample of the diluted exhaust taken from the tunnel and further diluted by filtered air in the chamber. The overall dilution of the exhaust by tunnel and chamber air was nominally 300:1, and the volume of the twice diluted sample was about 2100 cu ft. Details of the sampling probes, procedures for mixing and sampling, and measurement of dilution ratio in each run are presented in the Appendix, pages A-32 to A-42.

Instrumentation

A critically important part of the facility are the instruments for indicating and recording the composition of samples of exhaust and diluted exhaust, the ambient conditions, the operation of the cars, and the characteristics of the particles suspended in the exhaust gases. All instruments were selected with the objective of providing reliable and accurate analyses, checked periodically, given maintenance service as necessary, calibrated before each run, and then checked after each run to

(1) Habibi, Kamran, "Characterization of Particulate Lead in Vehicle Exhaust-Experimental Techniques", Environmental Science and Technology, Vol. 4, No. 3, March 1970, pp 239-253.

insure against unacceptable performance. Measurement techniques were evaluated and improved when possible throughout the experimental program. The carbon monoxide meter indicated carbon monoxide concentrations lower than the true values for Runs 4-11 to 4-26, (Table A-4), so that the cars ..ad CO emissions above the limits specified for the modified LA-4 cycle. Experimental data in this report give the true values for carbon monoxide concentration, corrected to compensate for the instrument error. The series of runs was repeated under conditions to give acceptable CO emissions, so that two sets of valid data were obtained for interpretation.

Three different oxygen meters of one type were used in the first half of the test program with recurring difficulties in achieving reliable operation and rapid response. After investigation a different type was substituted and used with completely satisfactory results.

In ten runs the size distribution of the aerosol particles in diluted exhaust in the residence chamber was measured with the Minnesota Aerosol Analyzing System (MAAS), a group of prototype instruments which quantitatively characterize aerosol particles in submicron size ranges and at low concentrations not accessible to other quantitative methods of measurement. Appropriate calibration procedures to standardize the data have not yet been worked out, so that the results given in this report are interpreted in relative terms to indicate the changes that occur in size distribution during aging of an aerosol by interaction of the particles with each other and with the walls of the residence chamber.

Two speed controllers were used during the experimental runs for automatic control of the driving cycle after the car was placed in gear. The first instrument was programmed by a punched paper tape, which was less precise than the magnetic tape program used in the later instrument, which resulted in a marked improvement in reliability and reproducibility.

Specific details of the instruments used and the calibration procedures are given in the Appendix, pages A-42 to A-47.

Filtration and Weighing

The mass concentration of solid particles in auto exhaust was measured by passing a measured volume of the diluted exhaust from the tunnel

through an absolute filter. If the filter retains only solid particles on its upstream face and passes all gaseous components, the increase in weight, ΔW, of the filter is then the weight of suspended particles collected from the filtered sample. ΔW is used to calculate the emission rate, R, of the car, as follows:

$$R = \frac{\Delta W}{D_{(LA-4)}} \times \frac{V(tunnel)}{V(sample)} \quad ,$$

where R is the rate of solid emissions, g/mile

ΔW is the weight gain of the filter when a constant sample stream is maintained during one LA-4 cycle

D is the distance driven during one LA-4 cycle, 7.5 miles

V(sample) is the rate of flow through the filter of a sample stream from the tunnel, cu ft/min

V(tunnel) is the rate of flow of diluted exhaust in the dilution tunnel, cu ft/min.

Ideally, sampling for particulates should be done isokinetically, i.e., the flow velocity entering the sample probe should be equal to the flow velocity in the tunnel. To accomplish this, the ratio $\frac{V(tunnel)}{V(sample)}$ should equal the ratio of the cross-sectional areas of the tunnel and the sample probe. However, when dealing with particulates in the submicron range such as normally found in auto exhaust, large deviations from isokinetic sampling can be tolerated (such as 10 to 1) without appreciable effect on the collection efficiency[1]. The deviation from isokinetic sampling, expressed as a ratio (Sampling Ratio) is given by the following equation:

---

(1) "Subisokinetic Sampling of Particles in an Air Stream", G. A. Sehmel, AEC Contract No. AT(45-1)-1830, Battelle-Northwest, March 1, 1966.

$$\text{Sampling Ratio} = \frac{\text{Actual Sample Velocity}}{\text{Isokinetic Sample Velocity}} =$$

$$\frac{V(\text{sample})}{V(\text{tunnel})} \times \frac{\text{Area (tunnel)}}{\text{Area (sample probe)}} .$$

The sampling ratios actually used in this program were 1.3 for the tunnel-to-chamber sampling, and 2.2 and 6.5 for the particulate sampling from the tunnel.

Experience in this study and discussions with other investigators have indicated that the weight change of a filter after filtration of dilute samples of auto exhaust can be affected by several experimental variables, such as the size of the sample line, the temperature of the sample stream at the filter, the face velocity of the sample stream, the size and type of filter, and the gross weight of filter relative to the weight of solid particles. Thus the real system used in these studies has required a major experimental study to develop and specify procedures that give a true value of ΔW.

This study has necessarily dealt with very small weights of collected particulate matter because of relatively large dilution ratios of about 30:1 in the tunnel and about 300:1 in the residence chamber. The size of the samples has been limited by controlling the flow rate through the filter to avoid excessive pressure drop, and by the short sampling time of 23 minutes during one LA-4 cycle. The weights of particles collected have ranged from a few milligrams down to less than a hundred micrograms. Particles were collected on two sizes of filters which weighed about 500 mg in 142-mm diameter, and about 70 mg in 47-mm diameter. A standardized technique had to be developed to measure weight gains that truly represented the amounts of solid particulate matter removed from the filtered air. The following requirements were included in the standard technique after development studies were completed.

- Microbalance with a sensitivity of better than 2 μg
- Control of atmospheric temperature and humidity in the weighing area

- Selection of abrasion resistant filter material
- Checks on operator technique by reweighing items of constant mass
- Discharge of static electricity from filters before weighing
- Duplicate simultaneous samples to detect and eliminate uncontrolled variables
- Parallel samples with two different membrane filter materials to detect any effects of filter medium composition
- A backup filter held in the same filter holder in contact with the primary filter and weighed after exposure to the same sample conditions, but without collection of the solid particles retained by the face of the primary filter. The weight change of the back-up filter is applied as a correction to the weight change of the primary filter.

The use of a backup filter is an important feature of the procedure used in these CRC studies. The data that support its use are reported in the experimental section. Details of application of other parts of the standard technique itemized above are given in the Appendix, pages A-47 to A-51.

EXPERIMENTAL RESULTS

Exhaust Emission Rates

The results of two series of runs are summarized in Table 1. These were carried out to examine reproducibility of the emissions with unleaded and leaded fuels. In the first series (Runs 4-11 to 4-26) a low reading caused by a malfunction in the electronic circuit of the CO analyzer permitted the actual gaseous emission levels of CO to be unintentionally higher than the limits specified for the LA-4 cycle of 47.0 g/mi CO. All data taken while the CO analyzer was malfunctioning have been corrected in Table 1 to give the real values during the tests.

Run Date	Test Conditions: Car	Fuel	Cycle	Schedule	General Comments	Emissions, g/mi: Part.+	HC	CO	NO_x++
4-4	W	NL	LA-4 (M)	I	Checkout	--	--	--	--
4-6	W	NL	LA-4 (M)	I	Checkout	--	--	--	--
4-7	W	NL	LA-4 (M)	I	Checkout	--	--	--	--
4-9	W	NL	LA-4 (M)	I	Checkout	--	--	--	--
4-10	W	NL	LA-4 (M)	I	Checkout	--	--	--	--
4-11	W	NL	LA-4 (M)	I	High HC, CO	0.192	5.81	68.8	2.46
4-12	W	NL	LA-4 (M)	I	High HC, CO	0.173	5.96	73.9	2.53
4-13	W	NL	LA-4 (M)	I	High HC, CO	0.195	6.13	72.5	2.88
4-16	W	NL	LA-4 (M)	I	High HC, CO	0.189	6.22	77.7	2.91
4-17	W	NL	LA-4	I-S	Std. Cycle	0.041	3.12	58.6	2.72
4-18	B	L	LA-4 (M)	I	Checkout only	--	--	--	--
4-19	B	L	LA-4 (M)	I	Aborted	--	--	--	--
4-24	B	L	LA-4 (M)	I	Aborted	--	--	--	--
4-20	B	L	LA-4 (M)	I	High HC, CO	0.319	6.07	71.9	1.99
4-25	B	L	LA-4 (M)	I	High HC, CO	0.349	5.94	68.2	2.06
4-26	B	L	LA-4 (M)	I	High HC, CO	0.340	5.76	75.8	1.90
5-9	B	L	LA-4 (M)	II	Baseline	0.135	3.91	34.1	2.60
5-10	B	L	LA-4 (M)	II	Baseline	0.153	5.35	47.4	2.21
5-11	B	L	LA-4 (M)	II	Aborted	--	--	--	--
5-14	W	NL	LA-4 (M)	II	Aborted	--	--	--	--
5-15	W	NL	LA-4 (M)	II	Baseline	0.040	3.43	35.5	2.35
5-16	W	NL	LA-4 (M)	II	Baseline	0.046	3.56	33.2	2.48
5-17	W	NL	LA-4 (M)	II	Baseline	0.044	3.99	38.5	2.50
5-18	W	NL	LA-4	II-S	Std. Cycle	0.075	4.66	52.4	2.47
5-19	W	NL	LA-4	II-S	Std. Cycle	0.071	4.12	46.8	2.49
5-21	B	L	LA-4 (M)	II	Baseline	0.211	3.37	38.2	2.19
5-22	B	L	LA-4 (M)	II	Baseline	0.203	3.46	44.1	1.93

KEY

Car: W - White; B - Blue
Fuel: NL - Nonleaded; L - Leaded
Cycle: LA-4 (M) Cycle with 55-second initial idle; LA-4 Cycle with 20-second initial idle
Schedule: Choke plate opening schedules defined on Pages A-14 to A-17

Particulate + Based on Metricel weights only, Sampling Ratio (actual velocity - isokinetic velocity)= 2.2

NO ++ Not corrected for humidity

Rather than use only the data with relatively high gaseous emission levels as baseline data for particulate emissions, new Choke Schedules II and II-S described in the Appendix (pages A-16 to A-17) were developed to lower gaseous emissions to acceptable levels. The baseline runs were repeated with modified LA-4(M) standard LA-4 cycles (Runs 5-9 through 5-22). These included a consecutive pair of baseline runs with the modified LA-4 (M) cycle on leaded fuel, a consecutive series with the modified cycle on unleaded fuel, and a consecutive pair using the standard LA-4 cycle with unleaded fuel.

Reproducibility of Mass of Particulate Emissions

Samples of diluted exhaust were taken from the downstream end of the tunnel and from the residence chamber during each of the ten Runs 4-10 to 4-26. Particles filtered from the samples were collected on two types of membrane filters. All samples used two filters assembled together in the same filter holder as a primary and a backup disk, according to the procedure described previously, to distinguish adsorbable vapors in the same stream. Each type of filter was used in duplicate filter holders and filter assemblies, so that four sample streams were filtered altogether.

Table 2 shows the mass of particles collected from the tunnel for each of the valid baseline Runs 4-11 to 4-26, and for each of the filter types to permit comparison with each other and with the gaseous emissions in the exhaust. Mean values and standard deviations are given for each filter type and each fuel. These comparisons show good agreement between filters and good reproducibility of particle emissions in repeated runs with the modified cycle. Emissions from the single run with the standard cycle are significantly lower than the emissions from the modified cycle.

Table 3 presents emissions data of Table 2 recalculated as mass concentration of particles, and includes the mass concentrations of particles sampled from the residence chamber immediately after a tenfold dilution and mixing of the tunnel sample, and after aging of the mixture for about 3-1/2 hours. The means and standard deviations, and coefficients of variation (CV, %) of each group of samples have been calculated for the modified LA-4 cycle operated with unleaded and lead fuel, using the two

TABLE 2. MASS EMISSIONS OF PARTICLES COLLECTED FROM TUNNEL BY FILTRATION
(Composite samples, dilution ratio, 30, one cycle, cold start)

			Emissions, g/mi				
			Particles on Filter Type				
Run No.	Fuel	Cycle	MET[a]	MIL[b]	CO	HC	NO
4/11	RE-141B Unleaded	Modified LA-4	.192	.204	68.8	5.81	2.46
4/12	Ditto	Ditto	.173	.178	73.9	5.96	2.53
4/13	"	"	.195	.214	72.5	6.13	2.88
4/16	"	"	.189	.208	77.7	6.22	2.91
Mean			0.188 ± .009	.201 ± 0.014			
4/17	"	Standard LA-4	.041	.043	58.6	3.12	2.72
4/20	RE-141C Leaded	Modified LA-4	.319	.285	71.9	6.07	1.99
4/25	"	"	.349	.360	68.2	5.94	2.06
4/26	"	"	.340	.386	75.8	5.76	1.90
Mean			0.337 ± .019	.344 ± 0.044			

(a) Metricel Filter DM450, Part No. 64519, Batch 80557, 142-mm, 0.45μm pore Flow 4.29± .10 cfm (Isokinetic flow rate 1.95 cfm).

(b) Millipore Filter AAWP 047 00 Lot 66499 15, 47 mm, 0.8 μm pore. Flow 0.70 cfm (Isokinetic flow rate 0.11 cfm).

TABLE 3. MASS CONCENTRATIONS OF PARTICLES COLLECTED FROM TUNNEL AND RESIDENCE CHAMBER

Run	Variables: Fuel	Variables: Cycle	Net Particulate Mass, g/m^3: Tunnel Composite MET	Tunnel Composite MIL	Residence Chamber Initial MET	Residence Chamber Initial MIL	Residence Chamber Aged 3-1/2 hr MET	Residence Chamber Aged 3-1/2 hr MIL
4/11	Clear 141B	Modified	2458	2600	215	317	356	--
4/12	Clear 141B	Modified	2208	2297	409	197	182	340
4/13	Clear 141B	Modified	2500	2753	302	394	248	336
4/16	Clear 141B	Modified	2419	2680	227	266	224	249
Mean			2389 ± 145	2582 ± 167	255 ± 113	293 ± 71	247 ± 74	308 ± 64
CV, pc			6.0	6.5	44.	28.	30.	21.
4/17	Clear 141B	Standard	526 ± 11	550 ± 28	98 ± 16	--	79 ± 6	--
4/20	Lead 141C	Modified	4090	3673	390	386	304	313
4/25	Lead 141C	Modified	4460	4638	448	491	348	367
4/26	Lead 141C	Modified	4362	4961	392	368	313	436
Mean			4304 ± 85	4432 ± 586	415 ± 34	409 ± 66	324 ± 24	372 ± 108
CV, pc			2.0	11.	8.	16.	8.	29.

types of filter paper. All entries in Table 3 are the mean of the net weight increase of duplicate simultaneous samples, each of which used two filters in a single holder. The weight change of the backup filter was applied as a correction to the particle weight collected on the primary filter, as described above (page 11).

These experimental data demonstrate the following characteristics of the specified method of filtration:

- The coefficient of variation (CV) of the mean particle mass from the tunnel was about 6 percent for both unleaded and leaded fuels.
- There is no significant difference between the two comparable means of the masses on the two types of filter paper from both the tunnel and residence chamber, even though the filter composition, area, face velocity, and total sample weight and volume for the two filter systems differed markedly.
- The backup filter provides a correction that eliminates uncontrolled variability related to face velocity at the primary filter, gaseous composition of the exhaust, and equilibration of the filter samples before weighings.
- The coefficients of variation of the residence chamber samples were higher than those of samples from the tunnel, because of the much smaller sample from the residence chamber.
- The mean values of the initial residence chamber samples were each in the expected range of 10 percent of the corresponding tunnel sample, agreeing with the tenfold dilution of the tunnel sample determined by gas analyses for CO and hydrocarbons.

Correlation of Light Scattering with Mass

Light scattered by the aerosol in the residence chamber was measured with an integrating nephelometer initially and after aging of the particles to determine the correlation of the light scattering coefficient with the mass of the suspended particles. Table 4 gives the light scattering coefficients and the mean mass concentrations of samples weighed on two types of filters for each of Runs 4-11 to 5-22. Figure 2 gives a plot of the straight line MASS in $\mu g/m^3 = 65.5\ (10^4\ b_{scat} - 0.4)$ that was calculated for minimum standard deviation ($\sigma = 0.59$) of residuals of all points. The intercept at $b_{scat} = 0.4$ is the measured background scattering of filtered air in the chamber. Correlation coefficient R of MASS with b_{scat} is 0.91. There is no apparent systematic influence of particles from either fuel type or aging because points in all categories fall around the regressed line. The correlation of auto exhaust light scatter measured in this study differs substantially from the Charlson correlation[1] $MASS = 38 \times 10^4\ b_{scat}$ for atmospheric dust, which is also shown in Figure 2. Charlson has found no deviations from his empirical experimental correlation, but he points out that it "may or may not hold in all cases". This is an instance in which either the light scattering of auto exhaust is less than for atmospheric dust, or the mass measured by filtration of exhaust according to the methods described above is greater than would be found by filtration of atmospheric dust with the same scattering coefficient. More investigation is necessary, but the empirical relation for auto exhaust may be useful before an explanation is found.

Addition of Foreign Materials to the Residence Chamber

Following the development of procedures and some shakedown runs, Runs 12-6 to 1-15 were carried out as summarized in Table 5 to investigate the effects of humidity in the chamber, lead in the fuel, dust and

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(1) Charlson, R. J., Ahlquist, N. C., Selvidge, H. and MacCready, P. B., Jr., Journal Air Pollution Control Assoc., Vol. 19, pp 937-942 (1969).

TABLE 4. CORRELATION OF LIGHT SCATTERING WITH AEROSOL MASS IN THE RESIDENCE CHAMBER

Run	Fuel	LA-4 Cycle	b_{scat} (10^{-4} m^{-1})		Mass, $\mu g/m^3$	
			Initial	3-1/2 hrs	Initial	3-1/2 hrs
4-11	Clear 141-B	Modified	5.0	--	266	--
4-12	Ditto	Ditto	4.6	--	306	--
4-13	"	"	5.5	1.8	348	292
4-16	"	"	5.5	--	247	--
4-17	"	Standard	1.5	--	98	--
4-20	Lead 141-C	Modified	6.0	--	388	--
4-25	Ditto	Ditto	7.2	6.9	465	358
4-26	"	"	6.4	6.2	380	375
5-15	Clear 141-B	Modified	1.4	1.1	84	--
5-16	Ditto	Ditto	1.3	1.4	70	49
5-17	"	"	1.2	1.2	50	19
5-18	"	Standard	1.9	2.1	95	56
5-19	"	Ditto	2.1	1.7	120	98
5-9	Lead 141-C	Modified	1.8	2.0	138	133
5-10	Ditto	Ditto	2.8	3.2	173	--
5-21	"	"	2.4	2.2	197	145
5-22	"	"	2.6	2.7	233	135

Nominal sample flow rate from tunnel to chamber = 10.0 cfm, isokinetic flow rate = 7.5 cfm.

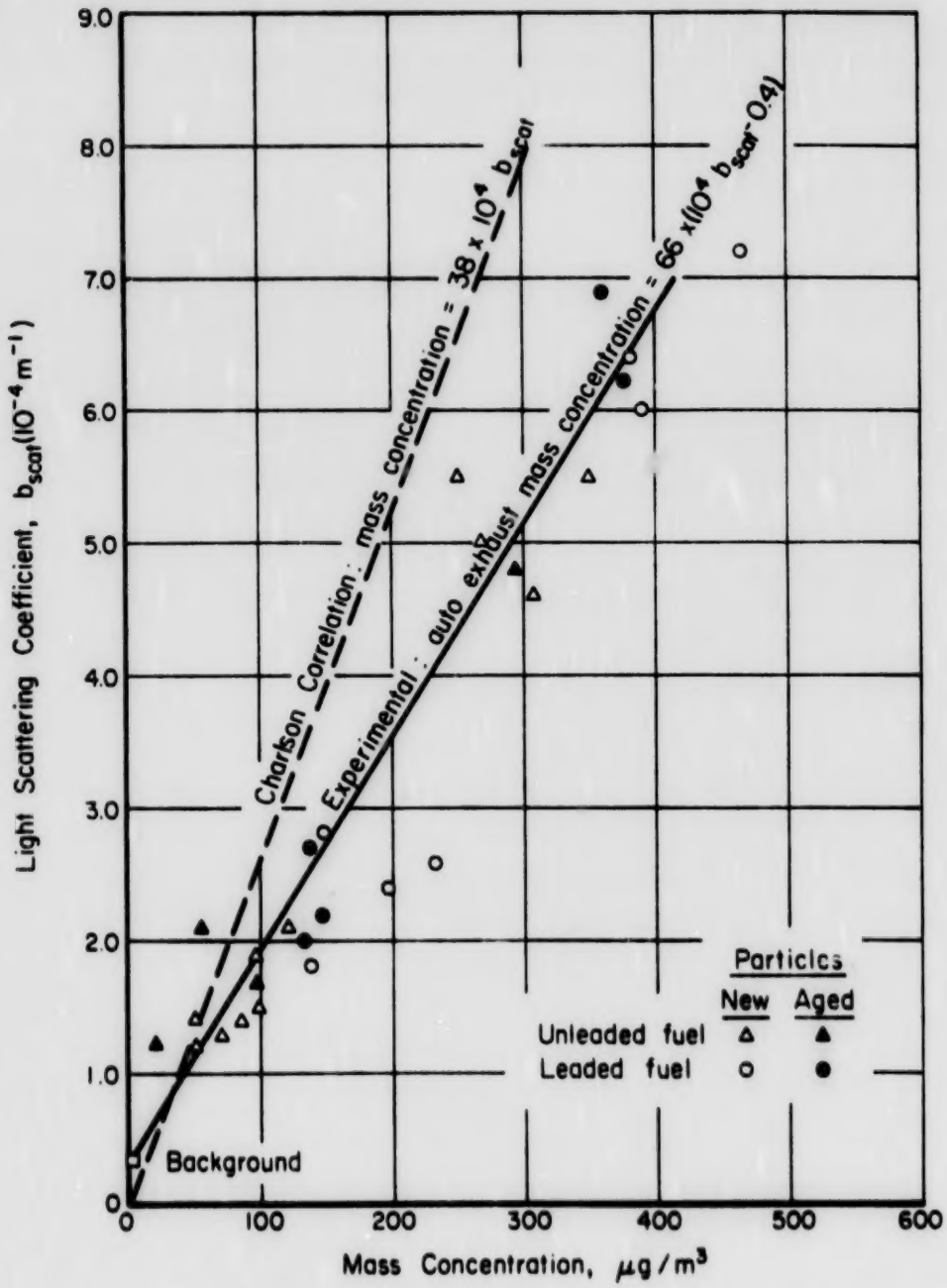


FIGURE 2. CORRELATION BETWEEN LIGHT SCATTERING AND AEROSOL MASS CONCENTRATION

TABLE 5. STUDIES OF ENVIRONMENTAL VARIABLES

Run Date	Test Conditions						General Comments	Variables				Emissions, g/mi			
	Car	Fuel	Cycle	Schedule	Controller	MAAS		Hum.	Lead	Dust	NH_3	Part*	HC	CO	NO
12-6	W	NL	LA-4 (M)	UD	DPC	Yes		O	O	O	O	0.011	1.98	3.3	2.81
12-13	W	NL	LA-4 (M)	UD	DPC	No	Soak temp low – NH_3 erratic	O	O	O	O	0.011	1.70	25.8	2.76
12-15	W	NL	LA-4 (M)	UD	DPC	Yes		O	O	O	O	0.014	2.06	22.1	2.49
12-18	W	NL	LA-4 (M)	UD	DPC	Yes	Soak temp low	O	O	O	O	0.018	1.63	27.2	2.52
12-19	W	NL	LA-4 (M)	I	DPC	No	CS changed – low CO idle	O	O	O	O	0.009	1.73	21.3	3.23
12-20	W	NL	LA-4 (M)	I	DPC	No		O	O	C	O	Dust	1.70	28.9	3.12
12-21	W	NL	LA-4 (M)	I	DPC	No		A	O	O	O	0.014	1.89	36.2	2.25
12-22	W	NL	LA-4 (M)	I	DPC	Yes		A	O	C	O	Dust	1.84	35.0	1.71
1-17	W	NL	LA-4 (M)	I	RI	No		O	O	O	O	0.038	1.69	32.6	1.46
1-19	W	NL	LA-4 (M)	I	RI	No		A	O	C	O	Dust	1.59	31.7	1.92
1-23	W	NL	LA-4 (M)	I	RI	Yes		O	O	C	O	Dust	1.40	29.2	1.36
12-27	B	L	LA-4 (M)	I	DPC	Yes	Various problems	A	B	C	O	Dust	--	--	2.23
12-28	B	L	LA-4 (M)	I	DPC	Yes	Run-in mileage low	O	B	C	O	Dust	5.95	58.1	2.17
12-29	B	L	LA-4 (M)	I	DPC	Yes		O	B	O	O	0.255	6.55	71.6	--
1-3	B	L	LA-4 (M)	I	RI	No	Run length low, idle CO low	A	B	C	O	Dust	4.82	31.0	2.53
1-5	B	L	LA-4 (M)	I	RI	No	Soak time short	A	B	O	O	0.241	7.23	58.1	--
1-10	B	L	LA-4 (M)	I	RI	No	Soak short, soak temp low	A	B	O	O	0.269	6.33	47.7	2.11
1-11	B	L	LA-4 (M)	I	RI	No	Idle CO high, soak temp low	O	B	C	O	Dust	5.36	33.4	1.96
1-12	B	L	LA-4 (M)	I	RI	Yes	Soak temp low	O	B	O	O	0.162	4.64	41.1	1.19
1-15	B	L	LA-4 (M)	I	RI	Yes		A	B	O	O	0.164	5.30	39.0	1.35

At this point the cars were leak checked and a small leak was found in the white car and a very small leak in the blue car.

Car W - White B - Blue
Fuel NL - Nonleaded L - Leaded
Cycle LA-4(M) Cycle with 55-second initial idle
Choke
Schedule UD Under development
I Defined in test
NO Nitrogen oxide - Values not corrected for humidity

Controller DPC Magnetic tape
RI Paper tape
Humidity (SI) Steam injection
Particulate + Based on Matricel weights, Sampling Ratio = 2.2
Variables O Low or normal values
A High humidity
B High lead
C High dust (solid impurity in atmosphere)
D High ammonia (gaseous impurity in atmosphere)

ammonia in the atmosphere, on the nature and fate of particles from the two matched cars. Residence time in the chamber was an independent parameter which was varied from about 1 to 24 hours.

Because the weighing procedure in the early stages was not as precise, and because of some operating malfunctions, the data are useful and valid only for interpretations given in following sections; broader interpretations should not be attempted. Subsequent runs with more definitive results have already been described in Table 1.

Size Distribution of Auto Exhaust Particles with the Cascade Impactor

No significant data on cumulative mass as a function of particle diameter were obtained when particles carried in the exhaust were separated into aerodynamic equivalent diameter fractions by passing a sample stream through six stages of the Battelle cascade impactor backed up by an absolute filter. The aerosol suspensions were too dilute and the time available for sampling was too short to build up weighable amounts of each fraction on individual impact stages. All stages gained weights in the range of a few to tens of micrograms, presumably because there was adsorption of volatile material as well as collection of solids by impact. Electron micrographs of collections on the impactor surfaces showed the particles were being classified by size. The morphology of particles in some of the size fractions is illustrated in a subsequent section.

The absolute filter, which retained unfractionated undersize with an equivalent diameter less than 0.25 μm, collected amounts of material weighing several hundred micrograms. Thus the predominant particles are in the size range below 0.25 μm.

Size Distribution of Particles with the Minnesota Aerosol Analyzing System

The Minnesota Aerosol-Analyzing System (MAAS) was used in ten tests, five with unleaded fuel and five with leaded fuel, as shown in Table 6. Size distributions indicated by MAAS for one selected run with each fuel are plotted in Figures 3 and 4.

TABLE 6. COMPARISON OF AUTOMOBILE PARTICULATE DATA

Test No.	Foreign Material	Filtration Mass Concentration, $\mu g/m^3$ Tunnel+	Residence Chamber Initial++	Residence Chamber 4 Hours	Light Scattering b_{scat} $(10^{-4} m^{-1})$, Initial	Light Scattering 4 Hours	MASS Instruments Particulate Vol. $\mu m^3/cc$ Initial	MASS Instruments 4 Hours
11-29	(a)	480	-	-	-	-	-	-
12-1	(a)	230	72.5	50	2.6	1.7	61	30
12-4	(ae)	172	42	-	2.9	2.6	386	241
12-6	(o)	290	27	18	0.82	0.85	-	-
12-15	(o)	176	37	40	0.95	1.0	36.4	35.9
12-13	(d)	137	38	33	0.70	0.88	-	-
12-18	(d)	169	24	6	0.65	1.10	19.7	68.5
12-19	(d)	121	10	37	0.52	1.15	-	-
1-17		492	91	40	0.65	0.65	-	-
12-21	(ad)	183	25	14	0.65	0.75	-	-
12-22	(ac)	3360	152	81	3.8	2.6	1152	356
1-23	(cd)	1869	-	-	3.6	2.7	-	-
12-20	(ce)	1645	94	85	2.5	2.2	-	-
1-19	(acde)	1608	-	-	3.3	2.3	-	-
1-5	(ab)	3088	233	236	5.7	5.1	-	-
1-15	(ab)	2100	120	145	2.4	2.5	262	163
12-29	(bd)	3260	271	213	5.5	4.6	697	422
1-12	(be)	2070	186	135	1.9	1.8	264	202
1-10	(abde)	3450	177	145	4.7	4.5	-	-
12-28	(bc)	6194	331	222	7.4	5.4	1228	476
1-3	(abcd)	4780	246	267	5.0	3.7	-	-
12-27	(abce)	20,240	1066	-	16.8	13.6	2786	1307
1-11	(bcde)	4818	221	238	4.25	3.3	-	-

(a) High humidity.
(b) Leaded gasoline.
(c) Arizona road dust contaminant.
(d) Ammonia gas contaminant.
(e) Long residence time.
(o) Represents all variables at low level.

+ Sampling Ratio = 2.2
++ Sampling Ratio = 1.3

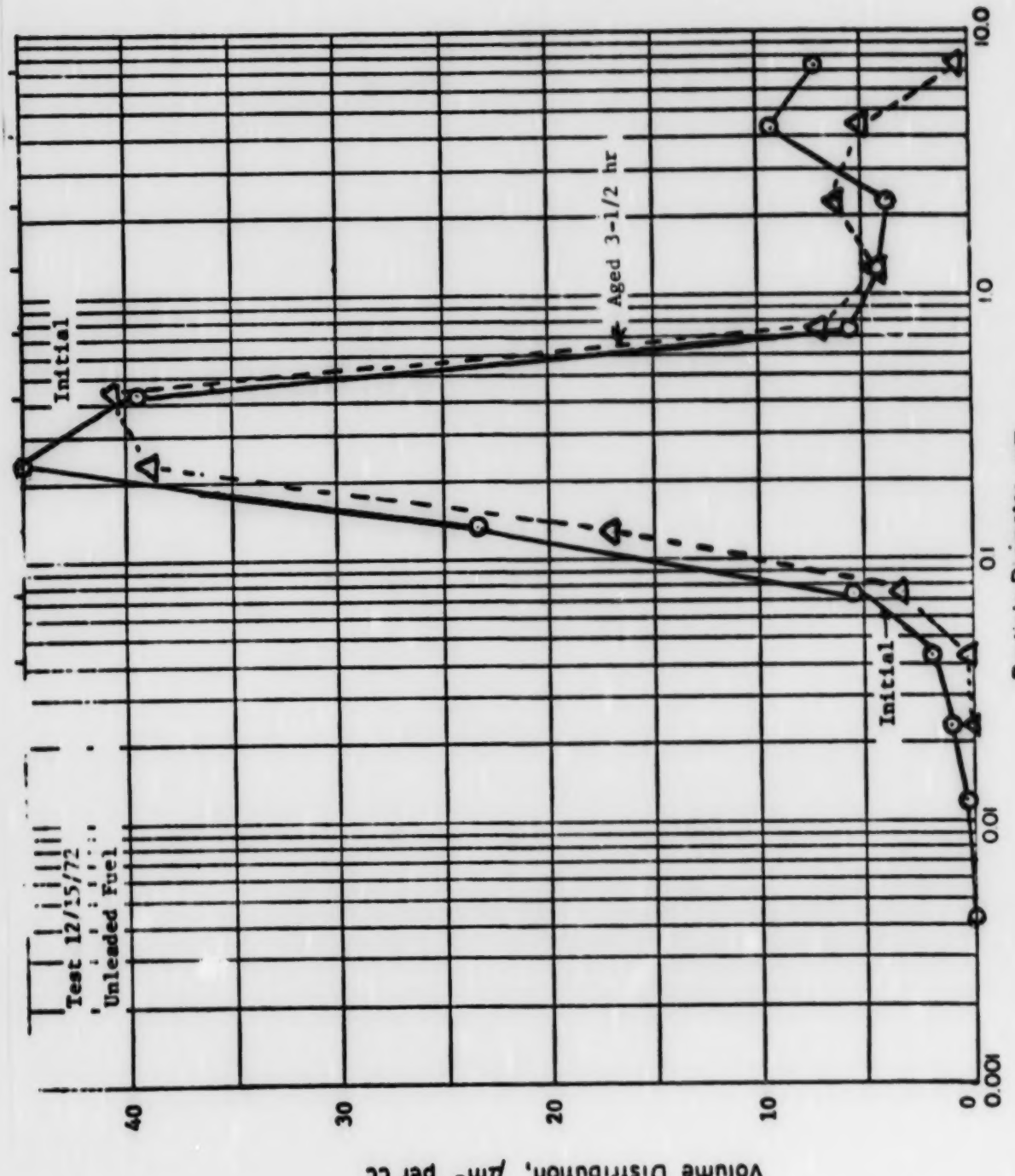


FIGURE 3. VOLUME DISTRIBUTION OF UNLEADED PARTICLES

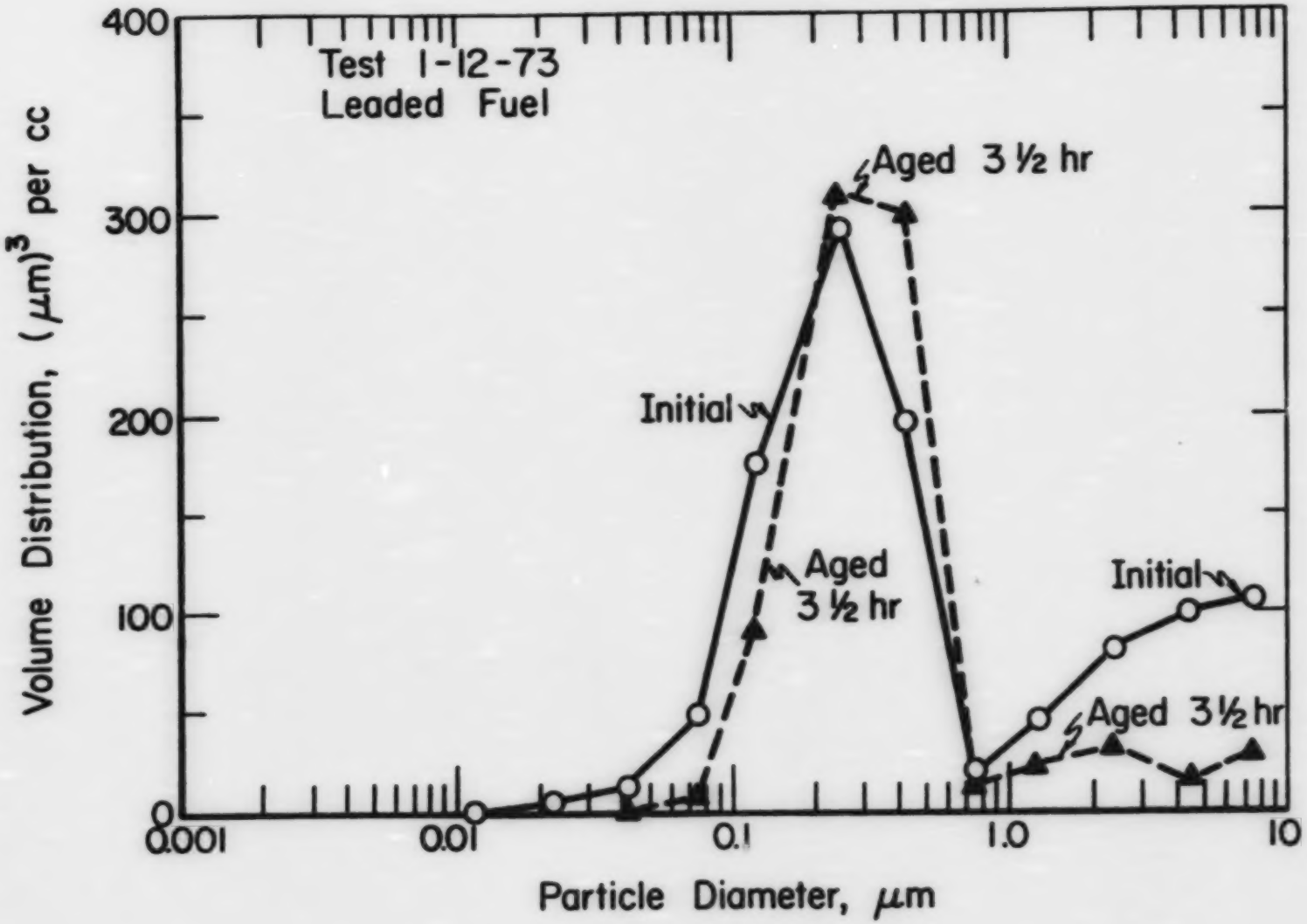


FIGURE 4. VOLUME DISTRIBUTION OF LEADED PARTICLES

Figure 3 (Run 12-15) shows the results obtained with unleaded automobile exhaust with no addition of any contaminant or humidity. The distribution changed little in 3-1/2 hours except for the removal of the very large particles and some growth in the small particles. Figure 4 (1-12) similarly shows some slight changes in 3-1/2 hours for the size distribution of leaded exhaust particles. The curves are similar in shape but differ greatly in the total volume of the two aerosols, since the ordinate scales differ tenfold. These are two single runs made with different choke schedules, so that the emissions found are not comparable as a typical difference in emissions from unleaded and leaded fuels. Multiple runs in each car under entirely similar controlled conditions must be made to obtain a significant comparison. The relative measurements of particles from unleaded and leaded fuels found by filtration and by MAAS instruments are sufficiently similar to encourage the use of both methods in detailed studies of the amounts and properties of particles.

Correlation of Particulate Mass with Hydrocarbon Emissions

A correlation was found between the mass rate of particle emissions and total hydrocarbon emissions, which is plotted as the curve in Figure 5 for unleaded fuel. The plot includes all of the data from all experiments (except dust injection runs), and one datum from an API study at Battelle with a so-called "warm start". The correlation is truly remarkable for unleaded fuel considering the many other parameters being varied. The leaded data do not correlate as well, particularly the three high humidity runs marked B, but the trend appears similar to that for the unleaded curve. The particulate emissions from the leaded fuel are from 0.05 to 0.15 g/mile above the nonleaded curve, or from 60 to 100 percent higher when compared at the same hydrocarbon emission level.

The reproducibility of the measurements of emissions in six sets of consecutive replicate runs was ±6.4 percent for particulate emissions and ±10.0 percent for gaseous emissions, expressed as the

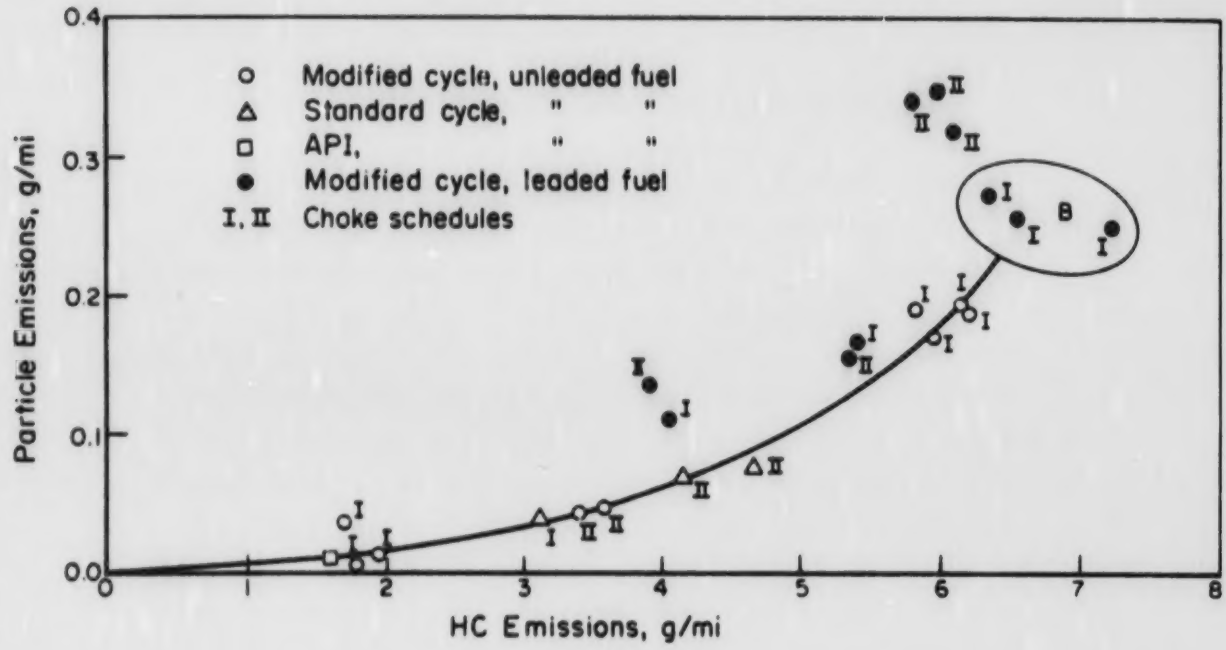


FIGURE 5. CORRELATION BETWEEN PARTICLE EMISSIONS AND HYDROCARBON EMISSIONS

unweighted mean of the percentage standard deviations of each set. These include all of the data on emissions in Table 1, page 13, except the single run on 4-17. Reproducibility after a longer period, such as 10 days between the duplicate pairs of Runs 5-9 and 5-10 and Runs 5-21 and 5-22, was not as good. This is the only such set of two pairs available for comparison, which precludes interpretation and definite conclusions.

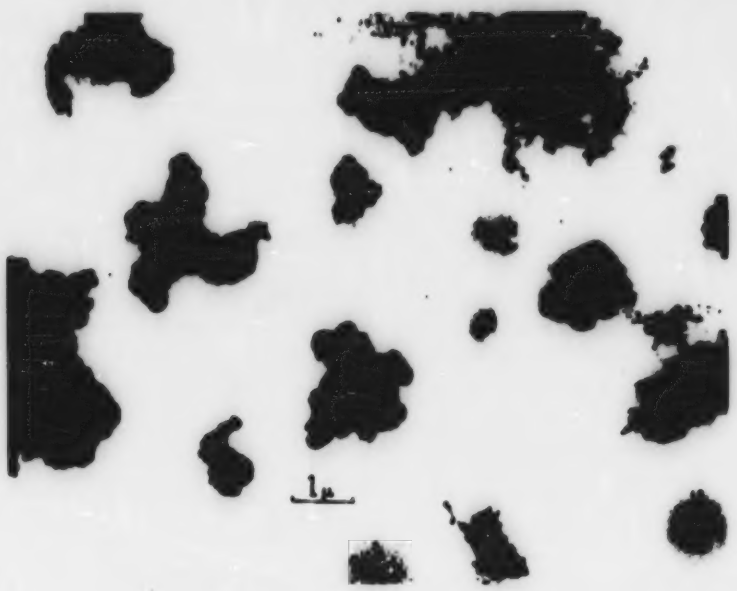
Morphological Characteristics of Particles

Exhaust particulates were collected by means of the cascade impactor directly onto electron microscope carbon support films on electron microscope grids. Without further specimen preparation the particles were examined in the transmission electron microscope.

In general, the same types of particles are seen, independently of the fuel used and the conditions of generation; agglomerates and aggregates are comprised of carbon black type material, condensate, and spherical fly-ash-like particulate matter. Figure 6 shows typical unleaded exhaust particles; there are several tar droplet particles which have low enough vapor pressure to persist in the vacuum system of the electron microscope under bombardment by the electron beam. Also, there is usually present a carbon-black-type structure of a chain-like aggregate, and fairly electron-dense particles which are cemented together with less dense material, which appears to have condensed around them.

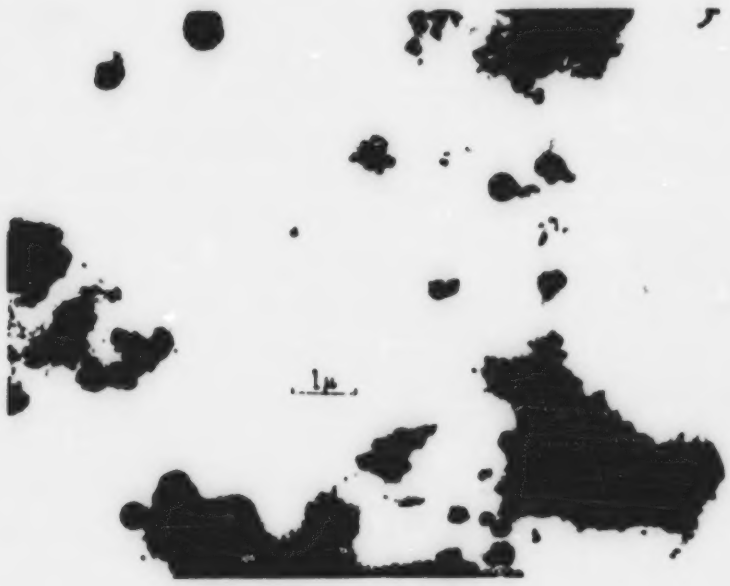
Figure 7 shows an electron micrograph of leaded auto exhaust. Carbon black and fly ash are cemented into aggregates by material which appears to have condensed around them. In some of the small aggregates, highly electron-dense structures are in evidence and probably are lead-rich.

Figure 8 is a group of four electron micrographs of unleaded particles from the residence chamber collected by the impactor in the two smallest stages, initially and after four hours of aging. The 0.25 μm stage has brushy and chain-like aggregates and many very small individual particles. After aging many more aggregates of a few particles each are visible. The initial sample at 0.5 μm is mostly spherical structures, several aggregated from three or four units.



J22216 10,000X

FIGURE 6. AN ELECTRON MICROGRAPH OF UNLEADED EXHAUST PARTICULATE COLLECTED AT THE 0.5-μm IMPACTOR STAGE AFTER 4 HOURS RESIDENCE (Run 4-17)



J22219 10,000X

FIGURE 7. AN ELECTRON MICROGRAPH OF LEADED EXHAUST PARTICULATE COLLECTED AT THE 0.5-μm IMPACTOR STAGE AFTER 4 HOURS RESIDENCE (Run 4-25)

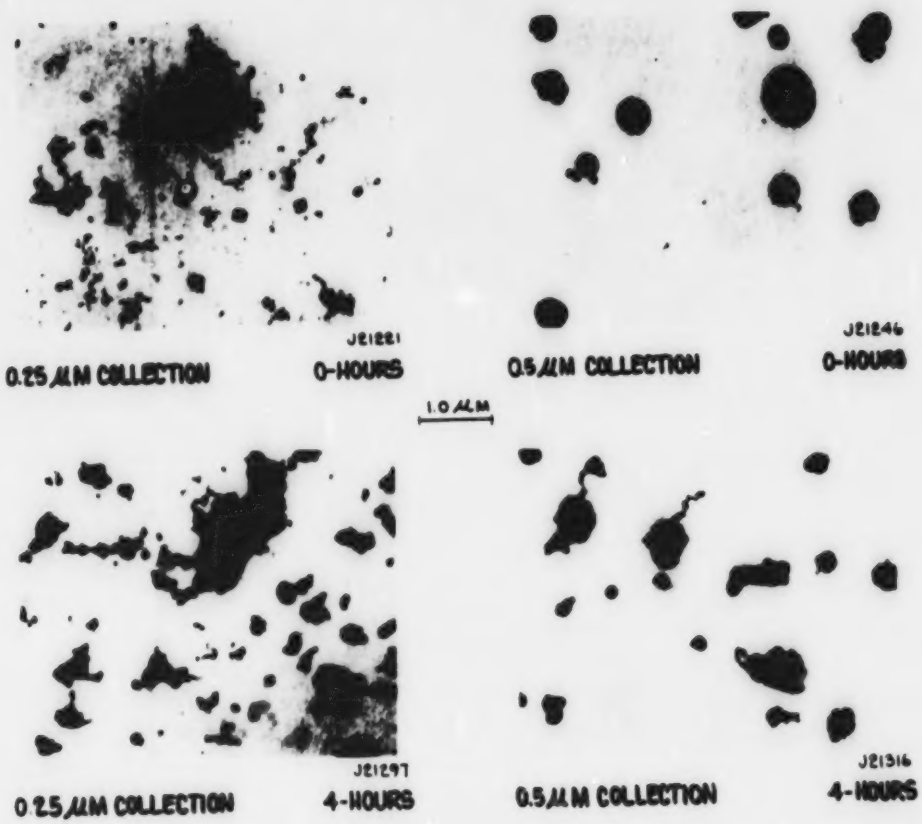


FIGURE 8. ELECTRON MICROGRAPHS SHOWING NONLEADED EXHAUST PARTICULATE FROM RUN 12-15

Figure 9 is another group of four views of particles from leaded fuel, not significantly different in shape and degree of aggregation from the unleaded particles of Figure 8.

Figure 10 shows four individual views of particles from the residence chamber with foreign materials also present. The dust contaminant added in Run 12-20 with unleaded gasoline persists for 20 hours of aging, and exhaust particles are not distinguishable from the dust. The presence of alkaline ammonia in the diluted exhaust of Run 12-13 from unleaded gasoline causes the growth of needles. A condensate layer appears to enclose aggregates of aged particles in the high humidity chamber atmosphere.

CONCLUSIONS

Emission Levels

(1) Particulate emission levels correlated very strongly with HC (and CO) emissions for the two fuels. For unleaded fuels, the level of hydrocarbon emissions appears to be the major significant factor correlating positively with particulate emissions.

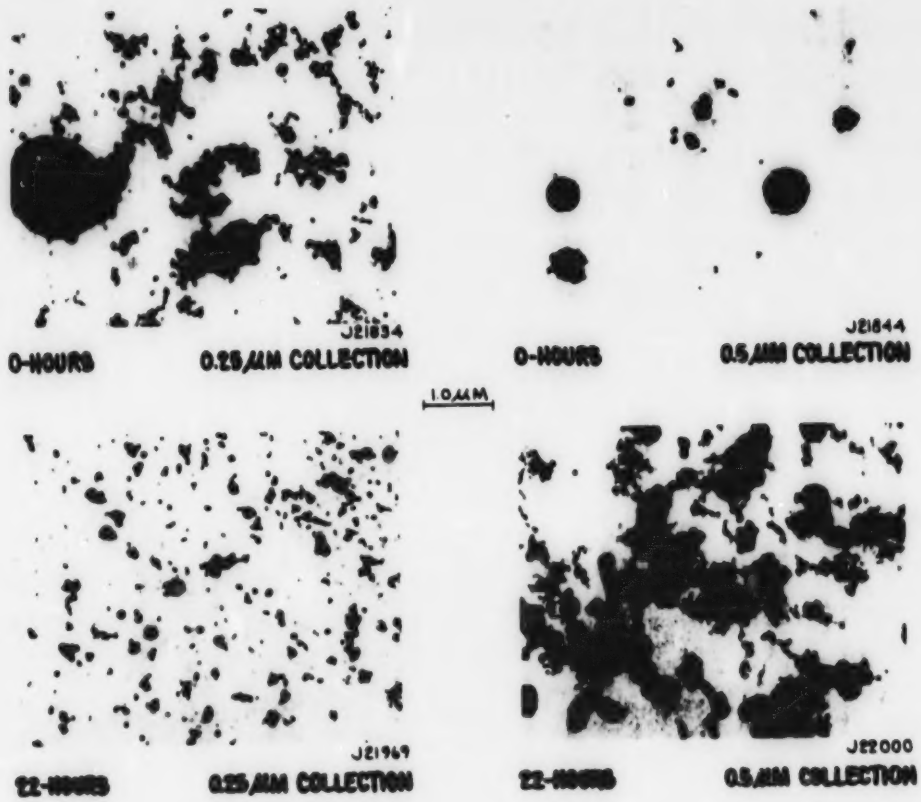
(2) The same choke schedule resulted in significantly different HC (and CO) emission levels for the two fuels.

(3) The same choke schedule resulted in significantly different weights of particulate emissions for the two fuels.

(4) For a given HC emission leaded fuel always gave higher weights of particulate emissions. For roughly equivalent gaseous emissions, the particulates from the leaded fuel are about 50 to 100 percent heavier than from the unleaded fuel.

(5) The reproducibility of the emission data on consecutive run days was a few percent.

(6) The determination of the particulate loading of the automobile exhaust is heavily dependent upon the characteristics of the sampling system and, in order to correlate results from different laboratories, there should not be any major differences in the filter media or sampling procedure.



KEY

RUN 12-28	RUN 1-5
RUN 1-15	RUN 1-15

FIGURE 9. ELECTRON MICROGRAPHS SHOWING LEADED EXHAUST PARTICULATE FROM SELECTED EXPERIMENTS

KEY

RUN 12-20	RUN 12-13
RUN 12-29	RUN 1-15

FIGURE 10. ELECTRON MICROGRAPHS SHOWING EFFECTS OF DUST, AMMONIA, AND HUMIDITY FROM SELECTED EXPERIMENTS

Particulate Characteristics

(1) Both the cascade impactor and MAAS (Minnesota Aerosol Analyzing System) indicated little difference in the particle size of the particulates from leaded or nonleaded gasoline. For the most part, the mass-median diameter of the dilute exhaust measured at the tunnel (30:1) was less than one-quarter micron. On the basis of the Minnesota System, the particle size distribution appeared to be bimodal.

(2) High humidity in the chamber produced no apparent effect on the size of the leaded particles; however, there was a considerable increase in the size of the unleaded particles.

(3) Ammonia caused no apparent increase in the particle size of the leaded particulates; however, there was a considerable increase in size of the unleaded particulates. Ammonia was the only additive to cause an increase in the particulate mass in the chamber as a function of time, and this effect occurred only for the unleaded particulates.

(4) The integrating nephelometer data for light scattering by the auto exhaust correlates directly with the mass data obtained by filtration. However, the slope of the correlation curve for auto exhaust is greater than the slope of the correlation curve proposed by Charlson for atmospheric dust.

Morphological Analysis

Four mechanisms of particle growth, listed in order of prevalence, were identified based on morphological studies of electron micrographs of the particles from both unleaded and leaded fuels.

First. Agglomeration

Almost every exhaust particle seen in the electron microscope can be classified as an agglomerate.

Second. Condensation

Many of the particles are surrounded by low density envelopes of what appears to be a condensate.

Third. Crystal Growth

Sometimes crystalline particles are detected, part of which are associated with oil or tar droplets.

Fourth. Ablation of Deposits

Particles larger than one micron and irregular in shape are likely to be chunks of material broken off exhaust system deposits.

The significant differences in particles from the two fuels were that the leaded particles frequently had an electron-opaque core, which undoubtedly represented a lead-rich nucleus; that agglomerates formed as a function of residence time; and that ammonia addition to the suspension of unleaded particles drastically affected their structure. The particles produced during runs in which ammonia was added to the dilution tunnel were highly irregular acicular structures, while in all other runs the particulates were generally spherical agglomerates.

A

APPENDIX

Fuels

TABLE A-1. CHARACTERISTICS OF FUELS[a]

Properties		Blend Designation[b] RE-141B unleaded	RE-141C Leaded
Research Octane No. (RON)		93.6	100.0
Motor Octane No. (MON)		85.4	91.7
Vapor Pressure, Reid, Micro (D-2551)		9.0	10.6
TEL as Lead, ppm (M-1059)		0.7	--
TEL as grams Pb/gal. (M-951)		(0.002)	2.49
Sulfur, % wt		0.036	(d)
Chlorine, ppm (M-600)		1.1	Present
Phosphorus, ppm (M-798)		<1.	1.
Nitrogen, ppm (M-1042, Col.)		21	21
API Gravity (D-287)		60.8	60.3
ASTM Distillation, °F	D-2887[c]	D-86	D-86
Initial Boiling Point	-16	93	92
5% Distilled	63	118	116
10% Ditto	77	132	130
20% "	142	156	154
30% "	188	182	178
40% "	207	207	202
50% "	231	228	223
60% "	241	244	240
70% "	275	260	256
80% "	292	286	284
90% "	335	331	330
95% "	369	366	374
End Point	--	400	403
C_5 & Lighter, Gas Chromatographic Analysis, wt - %			
Propylene		0.01	0.01
Propane		0.08	0.07
Isobutane		0.70	0.69
Isobutylene + Butene-1		0.07	0.06
n-Butane		5.00	5.02
trans-Butene-2		0.07	0.07
cis-Butene-2		0.09	0.09
3-Methylbutene-1		0.06	0.06
Isopentane		10.88	10.99
Pentene-1		0.16	0.16
2-Methylbutene-1		0.34	0.34
n-Pentane		2.56	2.59
trans-Pentene-2		0.41	0.42
cis-Pentene-2		0.22	0.23
Total C_5 & Lighter		(20.7)	(20.8)

TABLE A-1. (Continued)

Properties	Blend Designation[b] Re-141B unleaded	RE-141C Leaded
C_6 & Heavier, Mass Spec PONA, wt - %	43.8	43.6
Paraffins	3.9	4.0
Monoolefins	0.6	0.6
Cycloolefins & Diolefins	1.6	1.8
Monocycloparaffins	0.2	0.2
Dicycloparaffins	27.5	27.2
Alkylbenzenes	0.8	0.9
Alkylindanes & -tetralins	0.8	0.9
Alkylnaphthalenes	(79.3)	(79.2)
Total C_6 & Heavier		
Approximate Distribution of Alkylbenzenes by Mass Spec, wt - %		
C_6	1.8	1.7
C_7	6.9	6.5
C_8	9.0	9.1
C_9	6.8	6.8
C_{10}	2.2	2.2
C_{11}	0.8	0.8
C_{12}	0.1	0.1
Total Alkylbenzenes	(27.6)	(27.2)
Total Sample GC + MS PONA Summary, wt - %		
Paraffins	63.1	63.0
Olefins	5.9	6.0
Naphthenes	1.8	2.0
Aromatics	29.2	29.0
Grand Total CG & MS	100.0	100.0
Distillation-Chromatographic-UV Analysis		
Benz(a)anthracene	3.3 ppm	(d)
Benso(a)pyrene	1.0 ppm	(d)

Footnotes to Table A-1:

(a) Data supplied by Mobil Research and Development Corporation.

(b) Fuels RE-141B and RE-141C were prepared from a single 6000-gallon-lot which was composed of five blending components. Those components which tend to be unstable in long-term storage had antioxidant and metal deactivator (grades approved for use in military gasoline) added at the refinery.

Half of the 6000-gallon lot was put into clean drums and labeled RE-141B. The other half had Tetraethyllead Motor Mix added and, after mixing, was drummed, then labeled RE-141C. TEL Motor Mix contains ethylene dichloride (1.0 theory) and ethylene dibromide (0.5 theory) according to the usual specifications. No other additives were added during blending of either RE-141B or -C.

(c) Simulated distillation by gas chromatography of RE-141B.

(d) S, BaA, and BaP in RE-141C should be the same as that determined by analysis of RE-141B.

Air Flow Measurements

Figure A-1 shows measured engine air flow and road horsepower as functions of vehicle speed from idle (at 0 speed) to 60 mph.

Figure A-2 is a plot of air fuel ratio versus engine air flow showing the carburetor flow curve supplied by Ford Motor Company (dashed line) and the data calculated from tailpipe CO, CO_2, HC, and O_2 measurements. The two curves agree reasonably well up to 50 scfm (about 40 mph). At higher air flows the carburetor flow curve from Ford shows an air-fuel ratio higher by almost 1 A/F number. The reason for this is not known.

Car Maintenance

In preparation for each run, performance of the cars was observed and any necessary adjustment or maintenance was done.

After checkout runs were completed the oil was changed, a new oil filter and air filters were installed, points checked and cleaned, timing and dwell checked on both cars, and a series of 17 experimental runs (Runs 12-18 to 1-15) was completed. Then, the exhaust systems of both cars were pressure-tested at 1 psi for leaks. On the unleaded-fuel car a leak was noted at the joint between the Y-pipe and the muffler. A much smaller leak was noted at the same location on the leaded-fuel car. Both leaks were stopped by tightening the clamps. The cars were then not used for about 10 weeks while the data were examined in planning for the next series.

In preparation for the new series of runs the compression pressures on each engine were checked under motoring conditions. The results were as follows in order of cylinder number: unleaded-fuel car, 148, 158, 145, 146, 150, 155, 150, 150; leaded-fuel car, 155, 152, 150, 148, 133, 147, 150, 150. The compression in cylinder No. 5 in the leaded-fuel car is significantly lower than all other compression pressures. However, it is not low enough to indicate any major problem such as broken rings, stuck or warped valve, or burned valve seats.

Services on both project cars were: oil change, new oil and air filters, new spark plugs, points checked and cleaned, timing and dwell

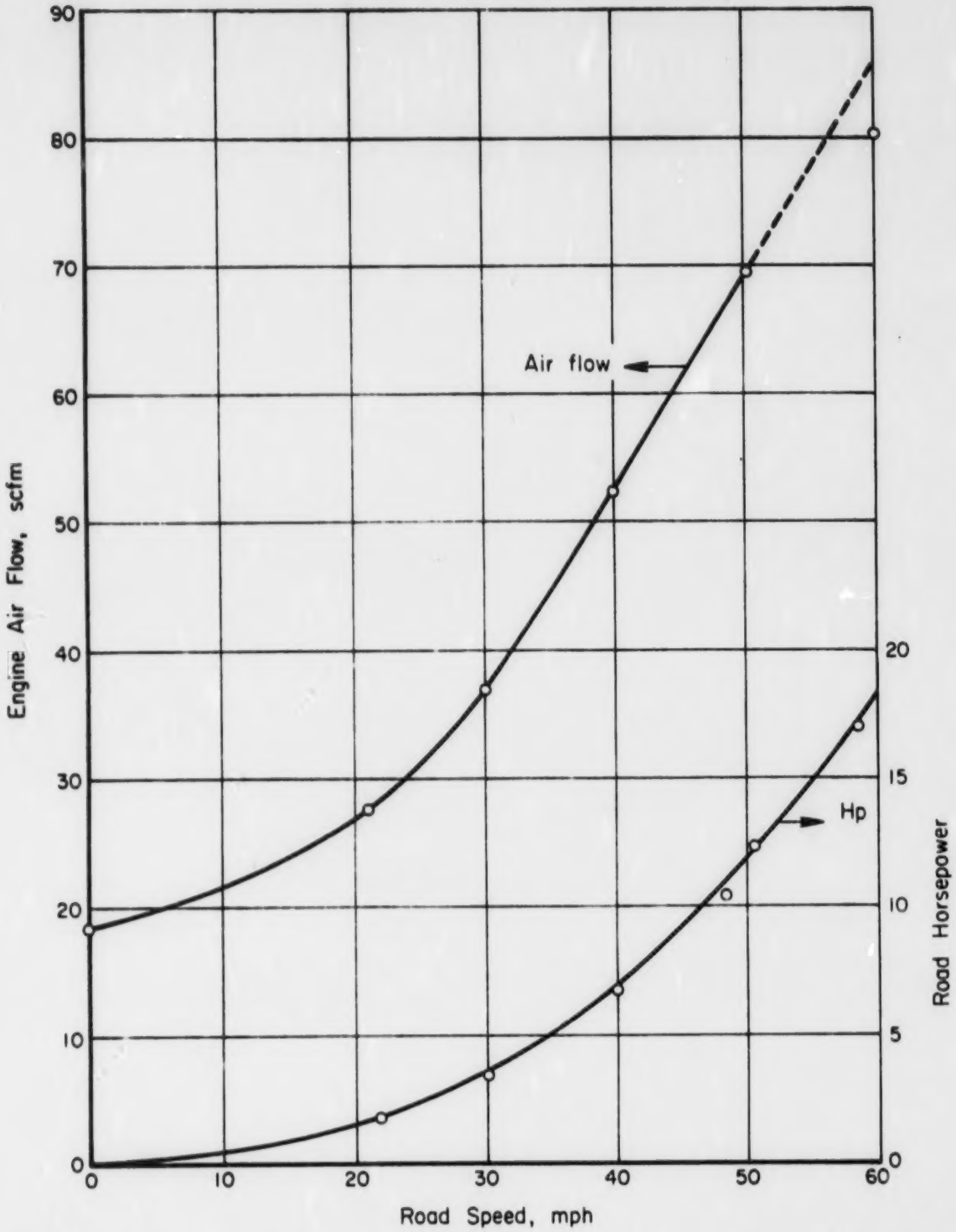


FIGURE A-1. VARIATION OF ENGINE AIR FLOW AND ROAD HORSEPOWER WITH VEHICLE SPEED USING UNLEADED FUEL

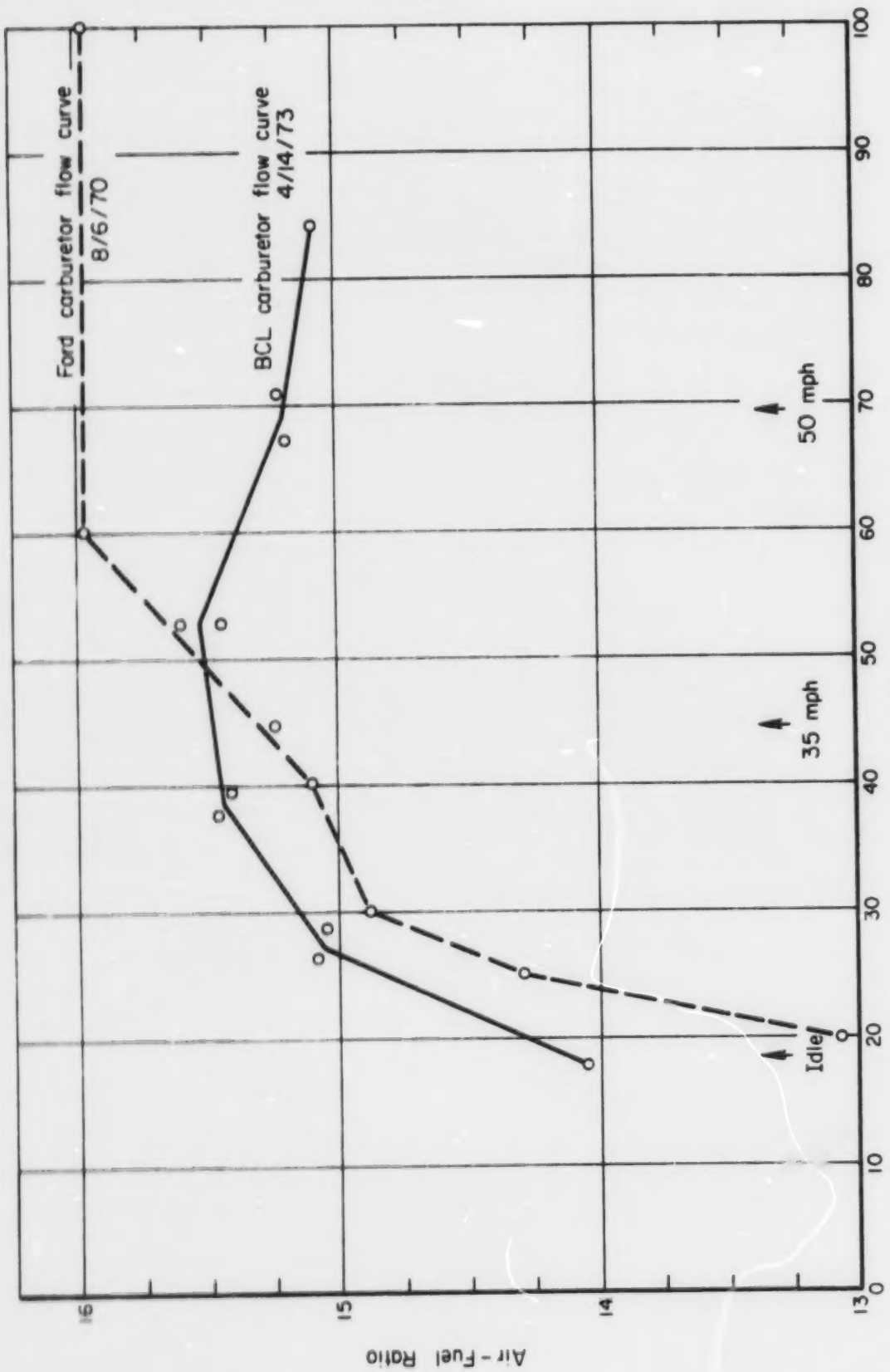


FIGURE A-2. AIR-FUEL RATIO VERSUS CARBURETOR AIR FLOW WITH UNLEADED FUEL

checked and set to specifications, and the ignition patterns were observed with an Ignition Analyzer. No problems or malfunctions were noted after servicing.

Oil Consumption

When the oil and oil filter in both cars were changed, the new oil and new filters were weighed before use. Following the test series the oil was drained and weighed again along with the filter.

Oil consumption by the unleaded-fuel car was 0.58 lb per 1000 miles over a total distance of 2,344 miles, and by the leaded-fuel car was 0.95 lb per 1,000 miles over a total distance of 1,212 miles. The oil density is 7.35 lb per gallon; thus, the oil consumption rate for the white unleaded car as shown in Table A-2 was 0.32 quart per 1,000 miles and for the blue leaded car was 0.52 quart per 1,000 miles.

In appearance, both oils were considerably darker after use than when fresh. Oil drained from the unleaded-fuel white car was black but not dirty in looks or feel. Oil from the leaded-fuel blue car was grey-black and looked and felt dirty.

Accumulated mileage at the beginning and at the end of the oil economy measurement was 10,583 miles and 12,927 miles, respectively, for the unleaded fuel car, and 9,217 miles and 10,429 miles, respectively, for the leaded fuel car.

After six test runs on the leaded-fuel car and ten test runs on the unleaded-fuel car, a check was made on the oil consumption. Oil consumption of the unleaded fuel car was 0.31 quart per 1,000 miles, and of the leaded fuel car was 0.39 quart per 1,000 miles.

Development of Acceptable Choke Operation

Apparatus

A device to move the choke plate automatically according to a preselected time schedule is illustrated in Figure A-3. A synchronous-type gearmotor driving a shaft with a tab on its end through an O-ring belt-and-

TABLE A-2. OIL CONSUMPTION DURING TEST SERIES (QUART PER 1,000 MILES)

Run No.	Unleaded-fuel car	Leaded-fuel car
11-29 to 1-15	0.32	0.52
4-4 to 4-26	0.31	0.39

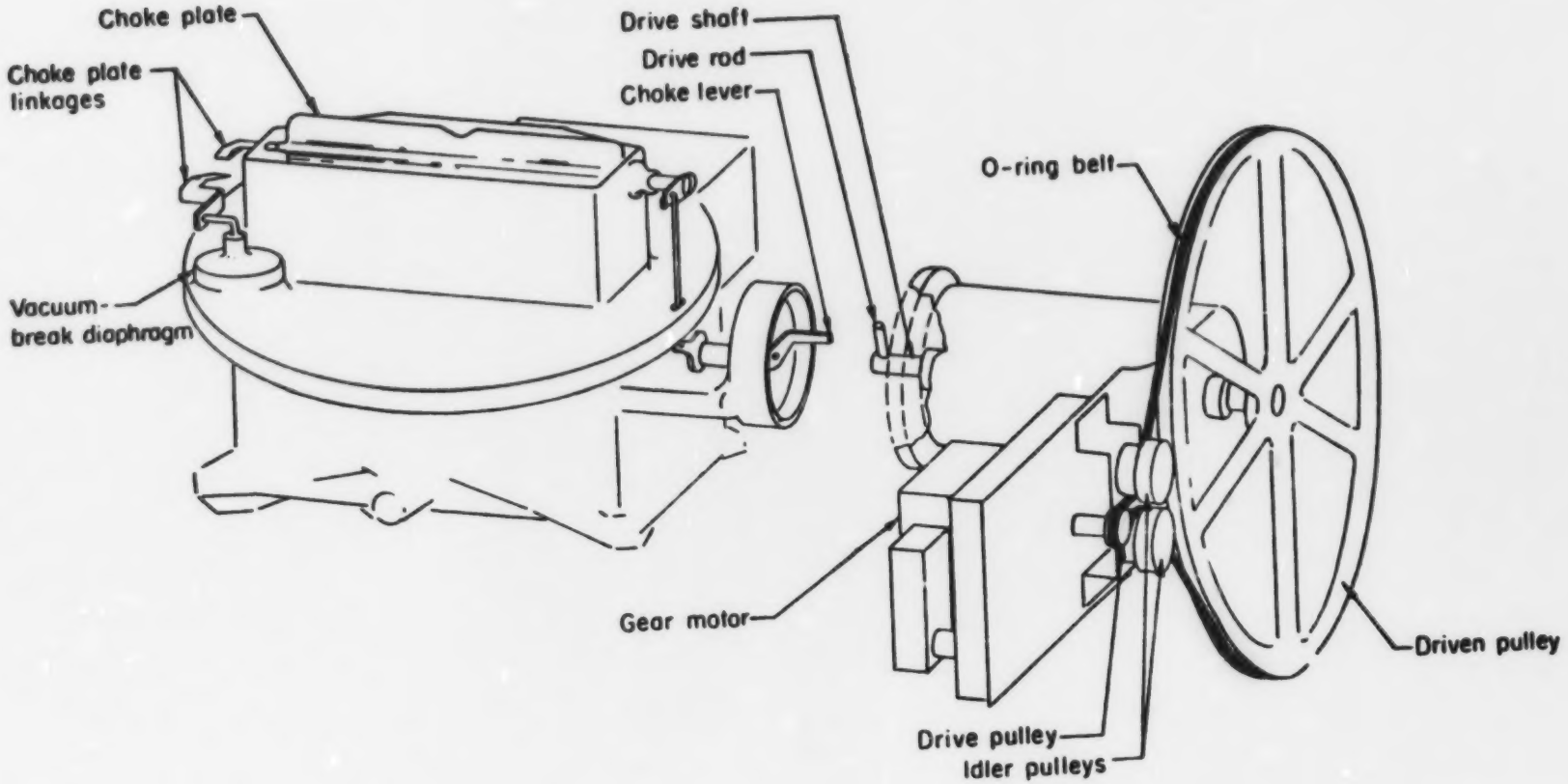


FIGURE A-3. **DEVICE FOR CONTROLLED CHOKE OPENING ON A REPRODUCIBLE TIME SCHEDULE**

pulley system was mounted on the choke housing, with the axis of the driven shaft coincident with the choke-plate shaft. The tab pushed against the choke lever in the choke housing to move the spring-loaded choke-plate shaft.

The gearmotor shaft speed was 1 rpm and the drive ratio was approximately 10 to 1. The shaft rotation rate is thus about 34 degrees per minute. Space limitations prevented using a higher drive ratio. To accommodate the gearmotor, drive ratio, and mounting housing and plate, the engine air cleaner housing was raised 1 inch from the carburetor body by means of a round spacer tube. Gaskets were used at each face of this spacer tube.

The choke is free to be opened wider than the control lever requires if intake-air velocity pressure is great enough to overcome the choke spring force. There was a lack of repeatability of the gaseous mass emissions during the series of Runs 12-19 to 1-15 inclusive, which may have been caused in part by too light a choke-plate spring resulting in erratic action due to the air velocity. Prior to resumption of testing with Runs 4-4 through 5-22 the automatic choke drive system was made more slip-proof by adding two idle pulleys which increased the O-ring belt tension and increased the contact length ("wrap") of the belt on both driver and driven pulleys. A stiffer spring was also installed on the choke-plate shaft to improve the stability of the choke plate under the influence of engine vibration and carburetor air flow. The lighter-than-normal spring had been used in the earlier series to minimize the chance of choke drive-belt slippage.

Characteristic Stages in Choke Schedules

There are three stages of choke motion. The first stage is a quick partial opening to about 30 degrees, as soon as sufficient manifold vacuum is present, which may require only 2 seconds. The second stage is a hold at partial opening while the thermostatic coil is warmed up by exhaust heat. The length of time at this stage depends on ambient temperature and the speed of thermostatic coil warmup. The third stage is under the control of the thermostatic coil and air velocity pressure on the choke plate. Time at this stage will depend on the design of the coil and the heat it receives.

Figure A-4 illustrates idealized choke-opening schedules for cold-start LA-4 cycles under various laboratory controlled conditions. Information used for the three solid curves on this chart was supplied to Battelle by Dr. W. R. Pierson of the Ford Motor Company and is derived from special development work conducted on Ford 351 CID engines. Real choke action is similar to the idealized curves in Figure A-4 but is not as sharply defined.

The lean and rich curves indicate limits within which a normal choke should be operated, for the particular engine and conditions of Ford's development program, to avoid stumble and stall at the lean end and to meet emissions standards at the rich end. These limits are only approximate and may be subject to wide variations with other cars, carburetors, or ambient conditions. Choke schedules developed in the experimental study of the CAPE-19 cars did differ, as shown in the next section.

Experimental Studies of Choke Schedules

Experiments with the choke opening schedule were conducted in conjunction with development and checkout of other systems, procedures, and instruments. Proper idle jet setting was also evaluated in these experiments. Initially, during a series of five runs, the idle jets were adjusted to give lean-side smooth idle at approximately 0.5 percent CO or less in drive idle. However, during later experiments, the drive-idle CO was raised to 1 percent. In the test program, the CO in drive idle was allowed to range between 0.6 and 1.2 percent or was readjusted to 1 percent.

Table A-3 summarizes the results of the test runs which were conducted in the process of developing the choke opening schedule. Three runs were made with the initial vacuum break angle of 30 degrees and with choke movement to full open at 70 degrees. Several tests were run at the 30 degrees vacuum-break angle but at several different time spans to full open. The vacuum break angle was then changed to 25 degrees for three more runs with a 3-minute time span to full open. Next, the vacuum break angle was reduced to 17 degrees. The time span to full open was kept at 3 minutes

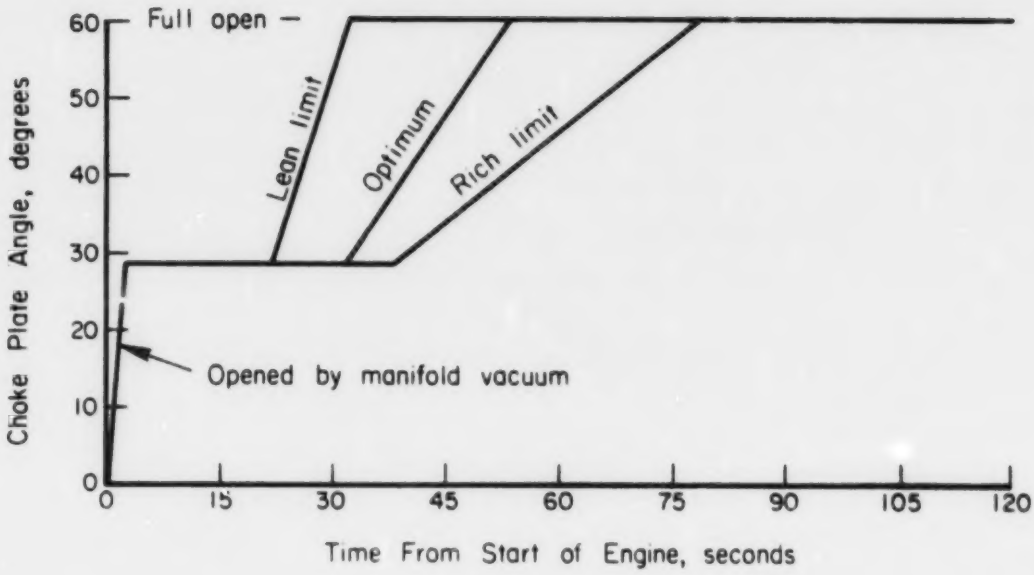


FIGURE A-4. IDEALIZED CHOKE OPENING SCHEDULES FOR MODIFIED COLD-START LA-4 CYCLE

TABLE A-3. TEST DATA RELATING TO CHOKE SCHEDULE DEVELOPMENT

Unleaded RE-141B Fuel
Tunnel Flow Rate 905 scfm
Sample Point Pressure 1 inch H_2O

	CO, percent[a]		Choke Schedule		Mass Emissions[d] g/mile		
			Vacuum Break[b]	Time Span to Full Open[c]			
Test No.	Idle	50 mph	Degrees	Minutes	HC	CO	NO
10-13	0.3	0.3	30	1.7	14.1[e]	11.1	3.31
10-16	0.2	0.3	30	2.7	11.7[e]	10.1	1.36
10-18	0.2	0.3	30	2.2	1.34[f]	9.9	1.56
10-25	0.2	-	25	3.0	1.38	13.3	2.97
10-26	0.4	-	25	3.0	3.96	19.6	1.55
11-15	1.0	0.5	25	3.0	2.09	11.9	2.82
11-16	0.7	-	17	3.0	2.18	54.3	2.93
11-17	-	-	17	3.0	1.95	25.6	2.89
11-29	0.6	0.4	17	3.8	2.02	30.4	2.88
12-1	0.6	0.5	17	3.8	2.30	34.0	2.93
12-4	0.7	0.4	17	3.8	2.06	26.3	2.63
12-6	1.1	0.5	17	3.8	1.90	38.6	2.81
12-18	0.8	0.4	17	5.3	1.63	27.2	2.82

(a) Measured at tail pipe.
(b) Full open choke is 70 degrees.
(c) Measured from start of engine.
(d) Computed from tunnel-bag gas composition.
(e) High HC emissions on Tests 10-13 and 10-16 indicated ignition system misfire problem, which was found to be partially shorted spark plugs.
(f) Ignition system problem corrected.

then increased to 3.8 minutes. Finally, a further modification was made in the choke schedule beginning with Run 12/18 to provide a slightly longer and also more realistic opening characteristic. The rate of opening was halved from about 32 degrees per minute to 16 degrees per minute. Also, the beginning of further opening from the vacuum-break position was advanced to about 2 minutes after zero time in the starting sequence and the full-open position was reached at about 5.3 minutes. This sequence was selected for use in the first tests and designated Schedule I, which completed choke-schedule experiments. Other schedules designated I-S, II, and II-S were selected later, to accommodate cycle changes and to maintain emissions within specified limits, as described in the next section.

Choke Schedules and Starting Sequences

Choke Schedule I (Modified LA-4 Cycle)

Figure A-5 shows Choke Schedule I. The sequence-time clock, exhaust-gas diverter valve, and tunnel bag and dilution air bag sampling are started simultaneously at time 0. Fifteen seconds later the engine is started. At 30 seconds the accelerator is "kicked down" and at 40 seconds the car is put in gear. The choke motor is started at 60 seconds (although the choke was opened 17 degrees by manifold vacuum when the engine started). The choke opening rate is 16 degrees/minute so the choke is full open (70 degrees) at 322 seconds (about 5.38 minutes). The first acceleration mode of the cycle begins at 55 seconds.

Choke Schedule I-S (Standard LA-4 Cycle)

Figure A-6 shows Choke Schedule I-S. The sequence-time clock, exhaust-gas diverter, valve, tunnel bag and dilution-air bag sampling, choke motor, and engine are started simultaneously. Ten seconds later the accelerator is "kicked down", and the car is put in gear at 15 seconds. The first acceleration mode begins at 20 seconds. The choke opening rate is 16 degrees per minute so the choke is full open at 262 seconds (4.38 minutes).

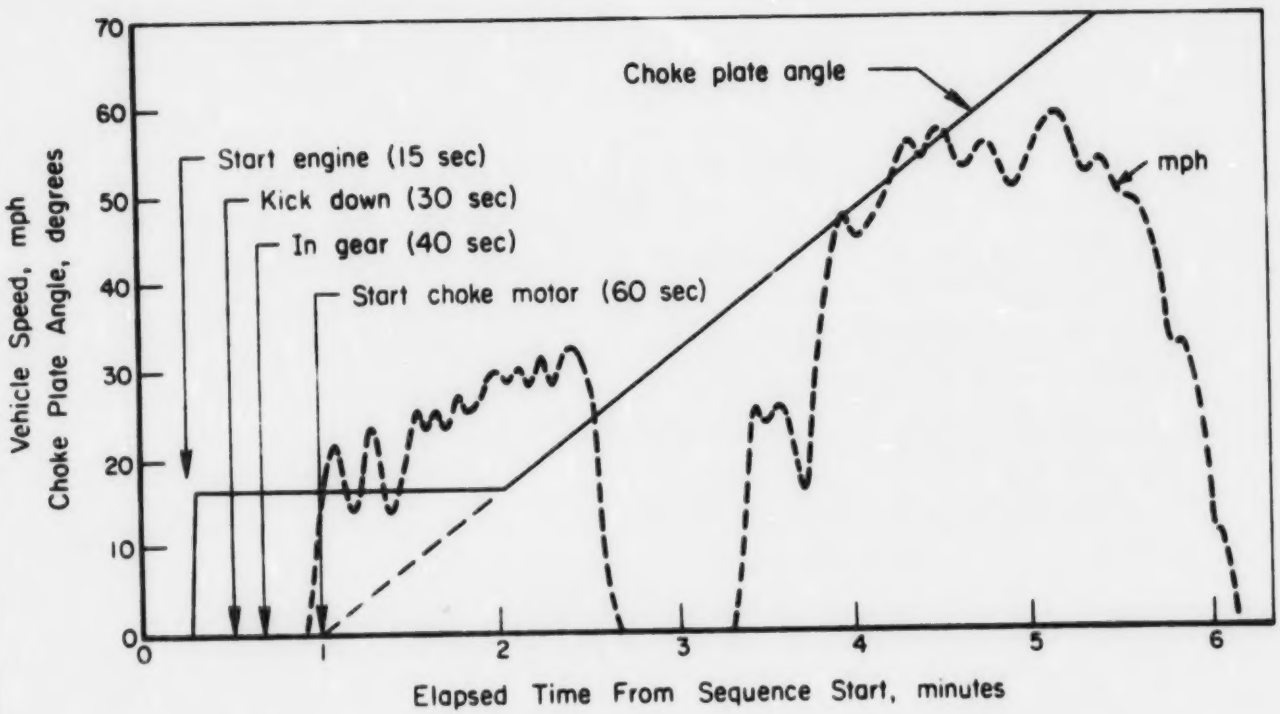


FIGURE A-5. CHOKE SCHEDULE I

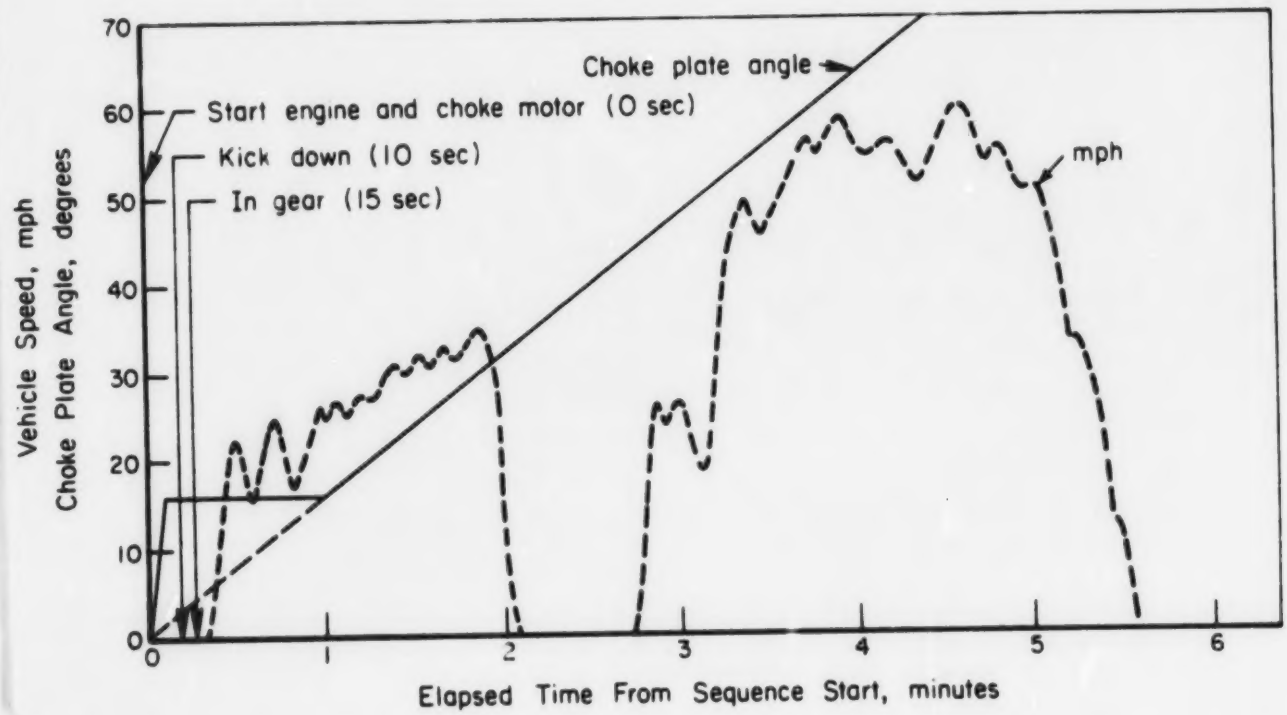


FIGURE A-6. CHOKE SCHEDULE I-S

Choke Schedule II (Modified LA-4 Cycle)

Figure A-7 shows Choke Schedule II. The sequence-time clock, exhaust-gas diverter valve, tunnel bag and dilution-air bag sampling, and choke motor are started simultaneously. Fifteen seconds later the engine is started. At 30 seconds the accelerator is "kicked down" and at 40 seconds the car is put in gear. The first acceleration mode begins at 55 seconds. The choke opening rate has been modified to 30 degrees per minute so the choke is full open in 140 seconds (2-1/3 minutes).

Choke Schedule II-S (Standard LA-4 Cycle)

Figure A-8 shows Choke Schedule II-S. The sequence-time clock, exhaust-gas diverter valve, tunnel bag and dilution-air bag sampling, choke motor, and engine are started simultaneously. Ten seconds later the accelerator is "kicked down", and the car is put in gear at 15 seconds. The first acceleration mode begins at 20 seconds, and the choke is full open at 140 seconds (2-1/3 minutes).

The dashed lines on Figures A-5, -6, -7, -8 represent the first and second modes of the driving cycle. Key events such as engine start, acceleration "kick down", and in-gear are identified.

Periods of Choke Schedule Use

Each of these schedules was developed to meet the requirements of stable car operation. Choke Schedule I and the corresponding starting sequence were used in Runs 12-18 to 1-23, 4-4 to 4-16, 4-18 to 4-26. Choke Schedule I-S was used for the standard LA-4 cycle of Run 4-17. Choke Schedule II was preferred for Runs 5-9 to 5-17, 5-21 and 5-22 to control gaseous emissions closer to the maximum allowable concentrations. Choke schedule II-S was adapted from II for two standard LA-4 cycle Runs 5-18 and 5-19. Other operational and apparatus information on these runs is summarized in the following section.

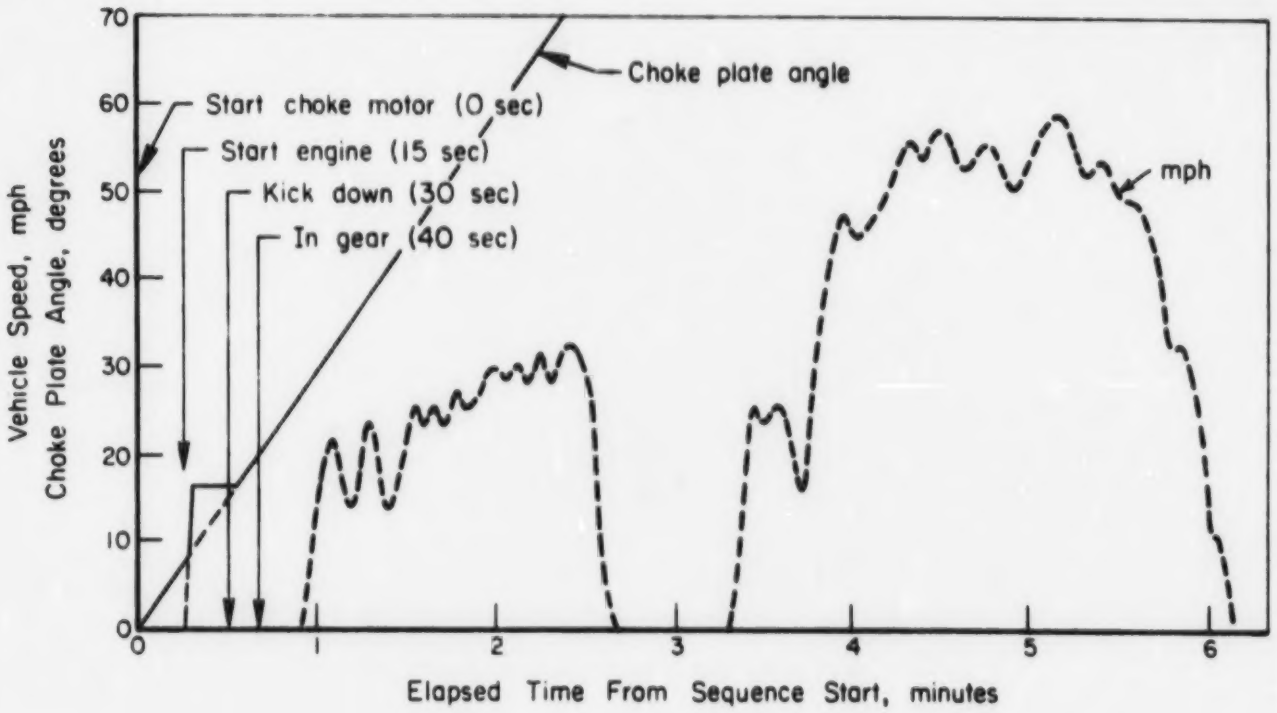


FIGURE A-7. CHOKE SCHEDULE II

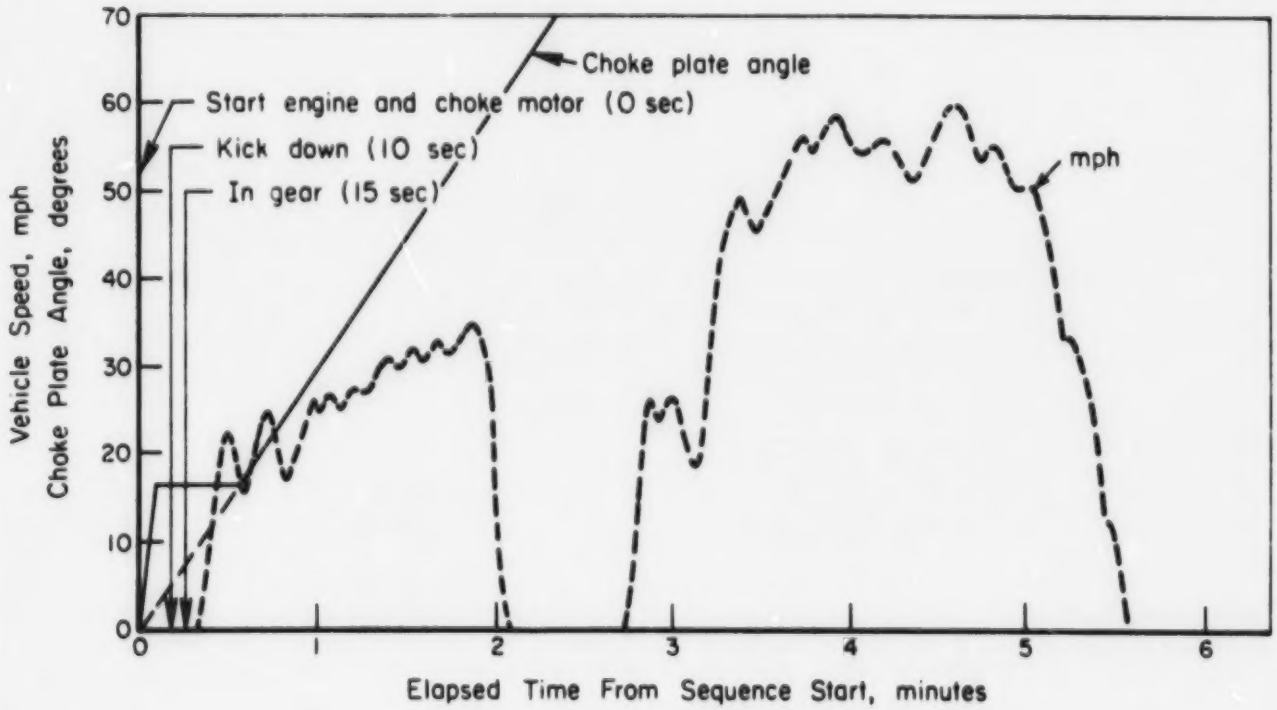


FIGURE A-8. CHOKE SCHEDULE II-S

Summary of Test Conditions in Experimental Runs

Table A-4 summarizes emissions of total particulates, HC, CO, and NO for the 58 experimental runs completed during the course of this study.

Dilution Tunnel

The dilution tunnel (Figure 1, page 3) is a steel tube 36 feet long and 23 inches in diameter constructed from six flanged sections bolted together. Dilution air is supplied by a blower to a filter section at the upstream end, and the filtered stream enters the tunnel near the tailpipe of the car. Exhaust and air both pass through a mixing orifice and thence through the tunnel to the sampling and outlet sections.

The tunnel outlet system consists of a 3-foot tapered section, a damper, and the discharge duct. The damper is used to control the pressure at the sampling point. The tapered transition section ahead of the damper assures that the tunnel flow patterns at the sample probes will not be affected by the flow restriction of the damper.

Sample Probes

The sample probes are located 30 feet 8 inches downstream from the mixing orifice. Figure A-9 is a cross-sectional sketch of the tunnel at the sampling point showing the location of the various sample probes and their function. Sampling ratios for the Sinclair-Phoenix smokemeter and single particle counter were 0.25 and 8.8, respectively, and the cascade impactor was operated at a sampling ratio of 9.2.

Figure A-10 is a detailed sketch of the residence chamber sample probe. This sample probe is a 2-inch (inside diameter) PVC plastic pipe enlarged to 2.1 inches at the inlet. The total length of the sample line is 8 feet with two large-radius bends, one in the tunnel as shown in the sketch, and one prior to entry into the residence chamber. The sliding-plate valve permits flow into the residence chamber when open and is used for precise control of the sampling time.

TABLE A-4. SUMMARY OF EXPERIMENTAL STUDIES OF EXHAUST EMISSION

Date	Test Conditions						General Comments	Variables				Emissions, g/mi			
	Car	Fuel	Cycle	Schedule	Controller	MAAS		Hum.	Lead	Dust	NH_3	Part*	HC	CO	NO
10-13	W	NL	LA-4 (M)	UD	RI	No	Ignition problems	O	O	O	O	--	14.1	11.1	3.31
10-16	W	NL	LA-4 (M)	UD	RI	No	Ignition problems	A (SI)	O	O	O	--	11.7	10.1	1.38
10-18	W	NL	LA-4 (M)	UD	RI	No		A (SI)	O	O	O	--	1.34	7.9	1.56
10-25	W	NL	LA-4 (M)	UD	RI	No	Choke development	--	O	O	O	--	1.34	13.9	2.87
10-26	W	NL	LA-4 (M)	UD	RI	No	Choke development	A (SI)	O	O	O	--	3.90	14.0	1.55
11-15	W	NL	LA-4 (M)	UD	RI	No	Choke development	--	--	--	--	--	2.09	11.9	2.82
11-16	W	NL	LA-4 (M)	UD	RI	No	Choke development	--	--	--	--	--	2.19	54.3	2.90
11-17	W	NL	LA-4 (M)	UD	RI	No	Manual drive	--	--	--	--	--	1.95	15.6	2.34
11-29	W	NL	LA-4 (M)	UD		No	Choke development	A (SI)	O	O	O	0.062*	2.02	20.5	2.88
12-1	W	NL	LA-4 (M)	UD	DPC	Yes	Low idle CO	A (SI)	O	O	O	0.031*	2.32	34.2	2.03
12-4	W	NL	LA-4 (M)	UD	DPC	Yes		A (SI)	O	O	O	0.015*	2.05	20.2	2.62
12-6	W	NL	LA-4 (M)	UD	DPC	Yes		O	O	O	O	0.021	1.98	30.3	2.81
12-13	W	NL	LA-4 (M)	UD	DPC	No	Soak temp low - NH_3 erratic	O	O	O	D	0.021	1.79	25.9	2.78
12-15	W	NL	LA-4 (M)	UD	DPC	Yes		O	O	O	O	0.034	2.06	32.1	2.49
12-18	W	NL	LA-4 (M)	UD	DPC	Yes	Soak temp low - CS changed	O	O	O	D	0.018	1.63	27.2	2.82
12-17	W	NL	LA-4 (M)	I	DPC	No	CS changed - low CO idle	O	O	O	D	0.003	1.71	29.3	3.23
12-20	W	NL	LA-4 (M)	I	DPC	No		O	O	C	O	Dust	1.70	26.9	3.12
12-21	W	NL	LA-4 (M)	I	DPC	No		A	O	O	D	0.014	1.89	36.2	2.25
12-22	W	NL	LA-4 (M)	I	DPC	Yes		A	O	C	O	Dust	1.84	33.0	1.72
1-17	W	NL	LA-4 (M)	I	RI	No		O	O	O	D	0.038	1.69	32.5	1.46
1-19	W	NL	LA-4 (M)	I	RI	No		A	O	C	D	Dust	1.59	31.7	1.91
1-23	W	NL	LA-4 (M)	I	RI	Yes		O	O	C	D	Dust	1.40	28.2	1.30
12-27	B	L	LA-4 (M)	I	DPC	Yes	Various problems	A	B	C	O	Dust	--	--	2.13
12-28	B	L	LA-4 (M)	I	DPC	Yes	Run-in mileage low	O	B	C	O	Dust	5.95	58.1	2.17
12-29	B	L	LA-4 (M)	I	DPC	Yes		O	B	O	D	0.255	6.35	71.6	--
1-3	B	L	LA-4 (M)	I	RI	No	Run length low, idle CO low	A	B	C	D	Dust	4.82	31.0	2.53
1-5	B	L	LA-4 (M)	I	RI	No	Soak time short	A	B	O	O	0.241	7.23	53.1	--
1-10	B	L	LA-4 (M)	I	RI	No	Soak short, soak temp low	A	B	O	D	0.269	6.33	47.7	2.11
1-11	B	L	LA-4 (M)	I	RI	No	Idle CO high, soak temp low	O	B	C	D	Dust	3.34	33.4	1.96
1-12	B	L	LA-4 (M)	I	RI	Yes	Soak temp low	O	B	O	O	0.102	4.04	44.1	1.19
1-15	B	L	LA-4 (M)	I	RI	Yes		A	B	O	O	0.164	5.39	39.0	1.38

At this point the cars were leak checked and a small leak was found in the white car and a very small leak in the blue car.

Table A-4. (CONTINUED)

Run No.	Test Sequence: Car	Fuel	Cycle	Schedule	Controller	Humidity	Simulated Conditions	Variables: Part.	Pb	Dust	$SO_4^=$	Emissions, g/mi: Part.*	HC	CO	NO_x
4-4	W	NL	LA-4 (N)	I	DFC	No	Clean car	0	0	0	0	--	--	--	--
4-5	W	NL	LA-4 (N)	I	DFC	No	Clean car	0	0	0	0	--	--	--	--
4-7	W	NL	LA-4 (N)	I	DFC	No	Clean car	0	0	0	0	--	--	--	--
4-8	W	NL	LA-4 (N)	I	DFC	No	Clean car	0	0	0	0	--	--	--	--
4-10	W	NL	LA-4 (N)	I	DFC	No	Clean car	0	0	0	0	--	--	--	--
4-11	W	NL	LA-4 (N)	I	DFC	No	High HC, CO	0	0	0	0	0.192	5.61	69.9	2.44
4-12	W	NL	LA-4 (N)	I	DFC	No	High HC, CO	0	0	0	0	0.173	5.96	73.9	2.32
4-13	W	NL	LA-4 (N)	I	DFC	No	High HC, CO	0	0	0	0	0.195	6.19	75.5	2.48
4-14	W	NL	LA-4 (N)	I	DFC	No	High HC, CO	0	0	0	0	0.189	6.22	77.7	1.91
4-17	W	NL	LA-4	I-S	DFC	No	4 Cycle	0	0	0	0	0.141	3.12	56.6	2.72
4-18	B	L	LA-4 (N)	I	DFC	No	Check at only	0	B	0	0	--	--	--	--
4-24	B	L	LA-4 (N)	I	DFC	No	Ab ted	0	B	0	0	--	--	--	--
4-26	B	L	LA-4 (N)	I	DFC	No	Ab ted	0	B	0	0	--	--	--	--
4-20	B	L	LA-4 (N)	I	DFC	No	High HC, CO	0	B	0	0	0.219	6.67	71.9	1.99
4-21	B	L	LA-4 (N)	I	DFC	No	High HC, CO	0	B	0	0	0.343	5.24	69.8	2.66
4-25	B	L	LA-4 (N)	I	DFC	No	High HC, CO	0	B	0	0	0.249	5.76	75.9	1.99
5-1	B	L	LA-4 (N)	II	DFC	No	Baseline	0	B	0	0	0.175	3.91	48.1	2.68
5-14	B	L	LA-4 (N)	II	DFC	No	Baseline	0	B	0	0	0.151	5.35	47.4	2.21
5-11	B	L	LA-4 (N)	II	DFC	No	Aborted	0	B	0	0	--	--	--	--
5-4	W	NL	LA-4 (N)	II	DFC	No	Aborted	0	0	0	0	--	--	--	--
5-15	W	NL	LA-4 (N)	II	DFC	No	Baseline	0	0	0	0	0.040	3.43	35.5	2.15
5-16	W	NL	LA-4 (N)	II	DFC	No	Baseline	0	0	0	0	0.046	3.50	31.2	2.48
5-17	W	NL	LA-4 (N)	II	DFC	No	Baseline	0	0	0	0	0.044	3.33	29.5	2.50
5-8	W	NL	LA-4	II-S	DFC	No	Std. Cycle	0	0	0	0	0.075	4.66	52.1	2.07
5-9	W	NL	LA-4	II-S	DFC	No	Std. Cycle	0	0	0	0	0.071	4.12	47.4	2.49
5-21	B	L	LA-4 (N)	II	DFC	No	Baseline	0	B	0	0	0.211	3.37	48.2	2.19
5-22	**B**	**L**	**LA-4 (N)**	**II**	**DFC**	**NO**	**Baseline**	**0**	**B**	**0**	**0**	**0.203**	**3.96**	**44.1**	**1.93**

KEY

Car	W - White	B - Blue
Fuel	NL - Nonleaded	L- Leaded
Cycle	LA-4 (N)	Cycle with 55-second initial idle
	LA-4	Cycle with 20-second initial idle
Schedule	UD	Under development
	I and I-S	Defined in text
	II and II-S	Defined in text
Instruments	MAS	Minnesota Aerosol Analysis System

Controller	DFC	Magnetic tape
	RI	Paper tape
Humidity	(SI)	Steam injection
Particulate	+	Based on Matricel weights, Sampling Ratio = 2.2
	*	Without backup filter
Variables	0	Low or normal values
	A	High humidity
	B	High lead
	C	High dust (solid impurity in atmosphere)
	D	High ammonia (gaseous

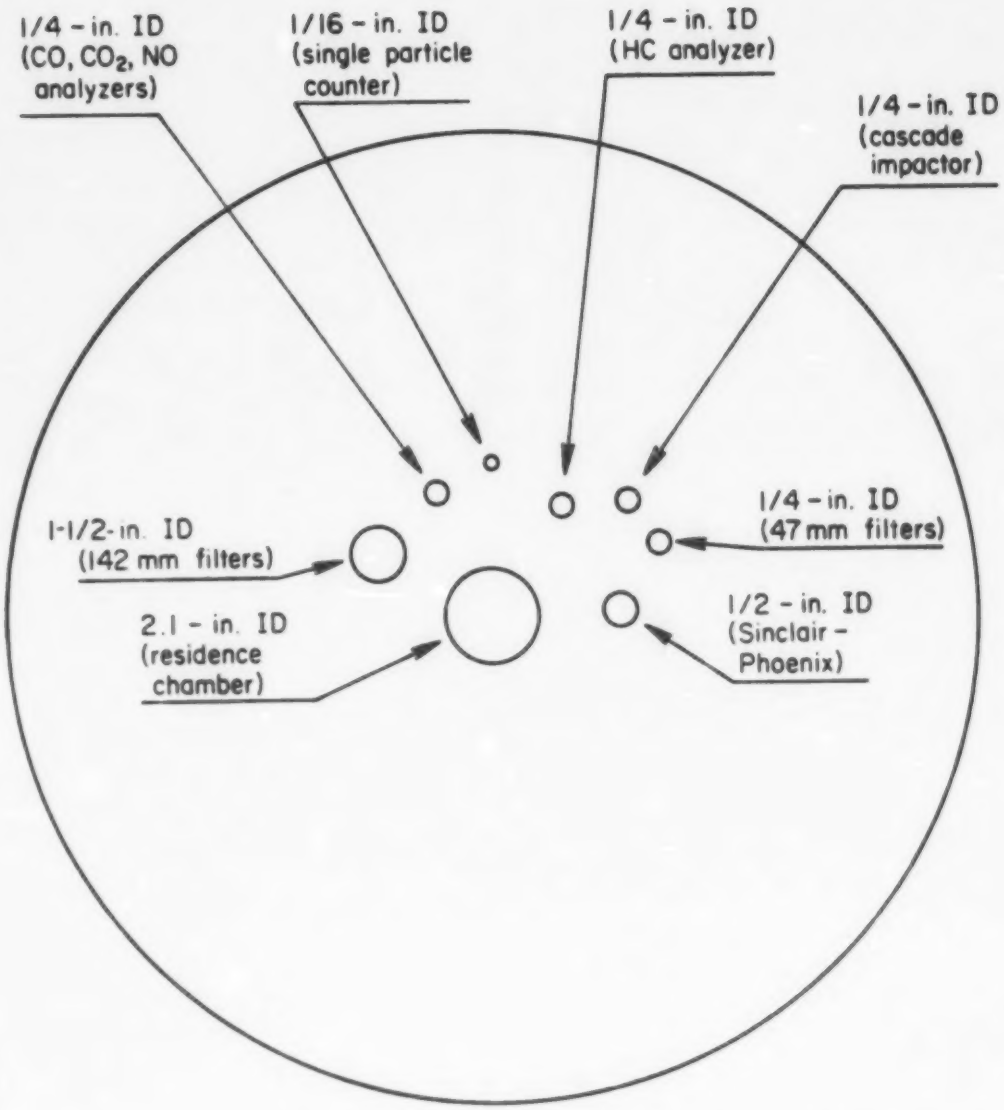


FIGURE A-9. PATTERN OF PROBE INLETS IN CROSS SECTION OF DILUTION TUNNEL AT SAMPLING POINT

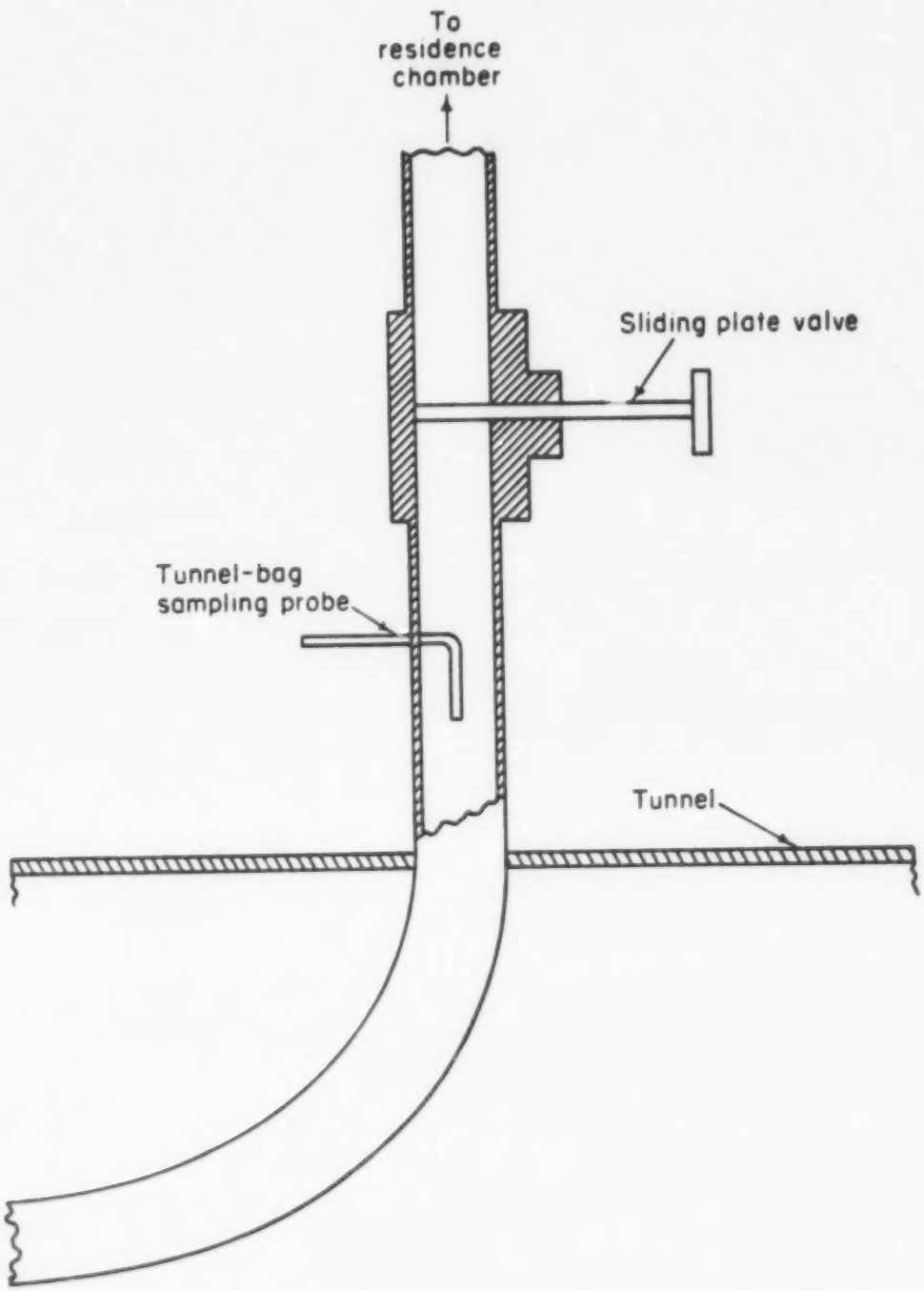


FIGURE A-10. CONNECTION AT TUNNEL OF PIPE TO CARRY DILUTED EXHAUST TO RESIDENCE CHAMBER

Tunnel Sample-Point Pressure

Operation of the tunnel at a positive pressure is necessary to provide a means for transferring sample from the tunnel to the residence chamber, which is always at ambient pressure because of its flexible walls. A further requirement of this sample-transfer operation is that the sample should always be proportional to the exhaust gases produced throughout the driving cycle. Since the tunnel flow rate is nearly constant, the sample flow rate should also be constant to achieve proportional sampling. The sample flow rate will be constant if there is a constant differential pressure between tunnel and residence chamber.

The differential pressure between tunnel and residence chamber was measured during a number of tests using a strain-gage pressure transducer with a range of 0 to 0.1 psi (2.77 inches H_2O). Tunnel sample-point pressures from about 1/2 inch H_2O up to about 2 inches H_2O were used. It was concluded from these tests that a tunnel sample-point pressure of about 1 inch H_2O results in an acceptably constant pressure differential.

Figure A-11 shows a reproduction of the chart record of tunnel-to-chamber differential pressure during a run in which the sample-point average pressure was 0.91 inch H_2O. The chart shows that ΔP remains acceptably constant throughout the cycle. Deviations from a steady pressure appear to be about ± 2 percent during most of the cycle. In the second high-speed mode of the cycle the tunnel pressure increased to about 10 percent over the average for a period of about 1 minute.

Tunnel-Bag Sample

A composite sample of the diluted exhaust gas is collected from the flow going into the residence chamber during the test run. This composite bag sample was analyzed for gaseous components to measure the final dilution from tunnel to chamber, as well as to monitor gaseous emissions for assurance of normal engine operation.

Figure A-12 is a sketch of the tunnel-bag sampling system. A diaphragm pump in conjunction with a rotameter and regulating valve supplies

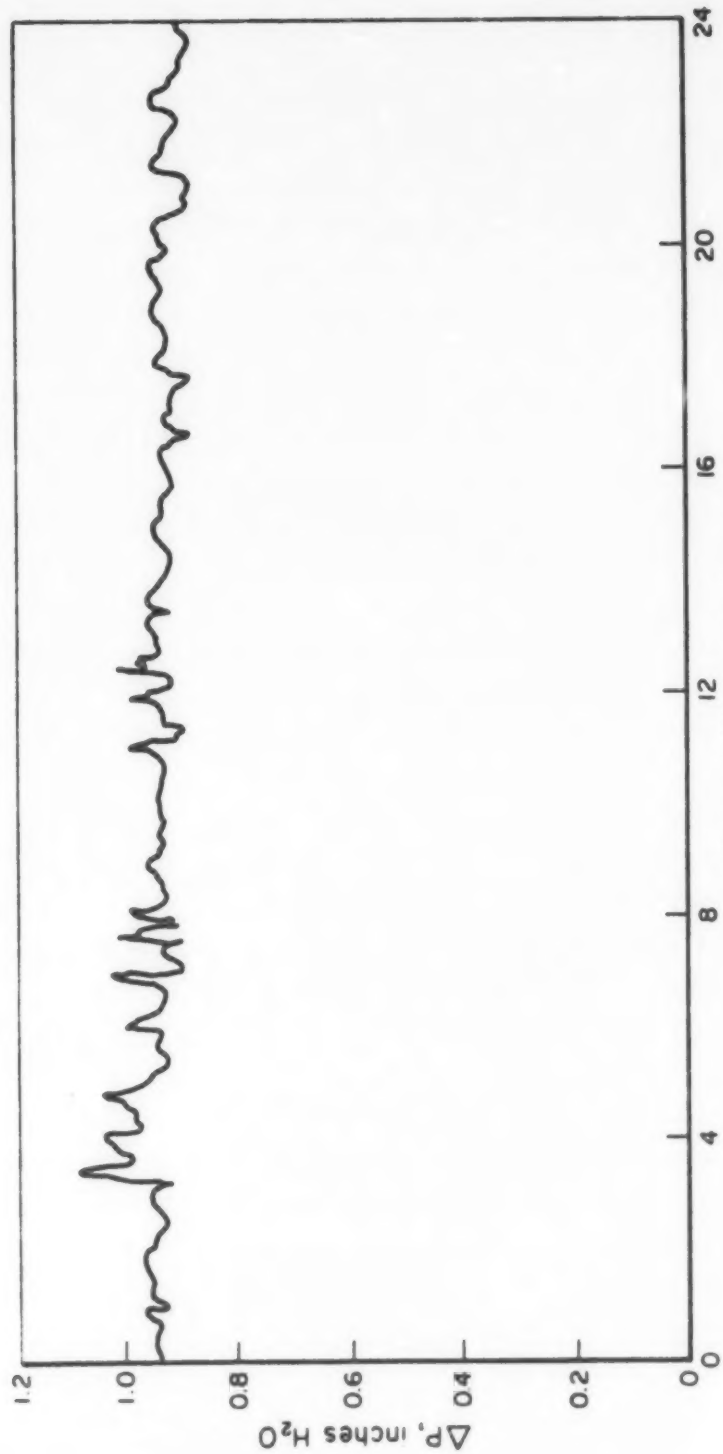


FIGURE A-11. RECORDED DIFFERENTIAL PRESSURE BETWEEN TUNNEL AND RESIDENCE CHAMBER DURING A MODIFIED LA-4 CYCLE

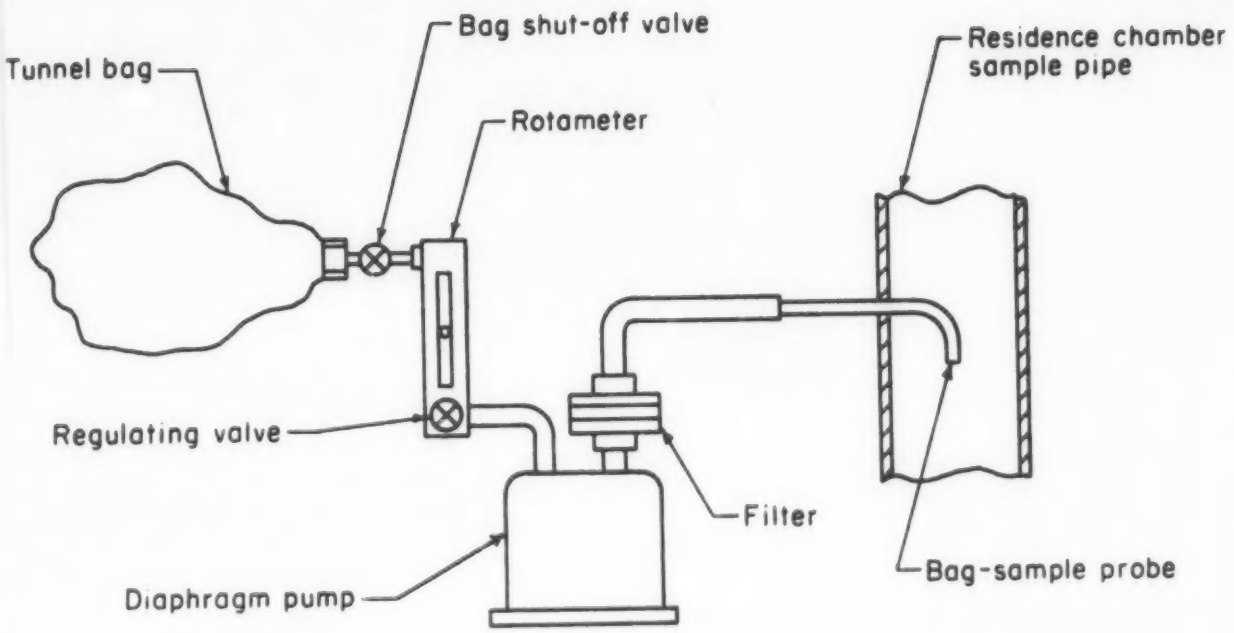


FIGURE A-12. TUNNEL-BAG SAMPLING SYSTEM

a constant sample flow rate to the bag. Particles are filtered out before the pump. At the end of the cycle the bag is disconnected from the rotameter and connected to the gas analyzers to measure the average gaseous emissions.

Calculation of Exhaust Mass Emissions from Tunnel-Bag Sample

A 23-1/2-minute bag sample of diluted exhaust gases from the tunnel is collected during each test run. This composite sample is equivalent to a CVS-type bag sample. Mass emissions per mile are computed as the product of contaminant density (g/cu ft at 68 F and 1 atm pressure) x contaminant concentration (vol/vol) x V_{mix}. The equation in the Federal Register[1] for calculating V_{mix}, the standard volume of the diluted exhaust gases emitted per mile, is as follows:

$$V_{mix} = \text{total tunnel flow rate (cfm)} \times \text{run length (minutes)} \times \frac{\text{tunnel absolute pressure (in. Hg)}}{29.92} \times \frac{528}{\text{tunnel temperature } (^{\circ}R)} \times \frac{1}{7.5 \text{ miles}} .$$

Lead Deposits in Pipe to Residence Chamber

Lead deposits were measured in the sample-transfer pipe between tunnel and residence chamber (Figure A-10, page A-22) after the pipe had been exposed to diluted exhaust from nine cold-start LA-4 cycles using leaded fuel. The operating parameters were as follows:

Fuel: 2.5 g Pb/gal; density, 6.25 lb/gal; rate, 4.25 lb/cycle Lead in fuel residues from nine cycles: 9 x 2.5 x 4.25/6.25 = 15.3 g

Sample Flow: Tunnel flow, 905 cfm; sample flow through pipe; 10 cfm (average values for all test runs)

Sampling Ratio: 1.3.

(1) Federal Register, Vol. 37, No. 10, January 15, 1972.

Assuming all lead is discharged in exhaust, then total sample flow in nine cycles contained 15.3 x 10/905 = 0.17 g Pb.

Found in sample pipe: 0.006 g Pb, or (.006/.17) x 100 = 3.5 percent of Pb in samples.

A particulate sample was collected on filters from the tunnel gas in Test 1-12 amounting to 0.006 g weight. Sample gas flows were 4.5 cfm through filters, and 10 cfm through pipe to residence chamber. Gas sample to chamber contained 0.006 x 10/4.5 = 0.013 g particles. Assuming the exhaust particles contained a mean value of 25 percent Pb, and that this test was typical of nine leaded fuel tests, total lead carried through the pipe was 0.013 x 9 x .25 = 0.029 g. Sample collected from wall was (.006/.029) x 100 = 21 percent of Pb exposure, based on the assumptions made.

It is concluded from these results that lead loss in the transfer of sample gas to the residence chamber is a significant part of the total particulate sample, and would affect a quantitative material balance. Nevertheless, losses are not so severe as to preclude study of aging of particles in the residence chamber.

Test for Uniformity of Mixing in the Tunnel

Simultaneous samples of auto exhaust particles were collected at the standard sampling location (Page A-18) from a 13-probe assembly to measure the uniformity of particle distribution across two perpendicular diameters of the tunnel. The coefficient of variation was 4.5 percent, which is an acceptably uniform distribution.

Gaseous Contaminant Injection System

Figure A-13 is a sketch of the gaseous contaminant injection system, which was installed for the study of the effect of a gaseous contaminant, ammonia, on aging of auto exhaust particles in the residence chamber. The gaseous contaminant is introduced into the tunnel for mixing

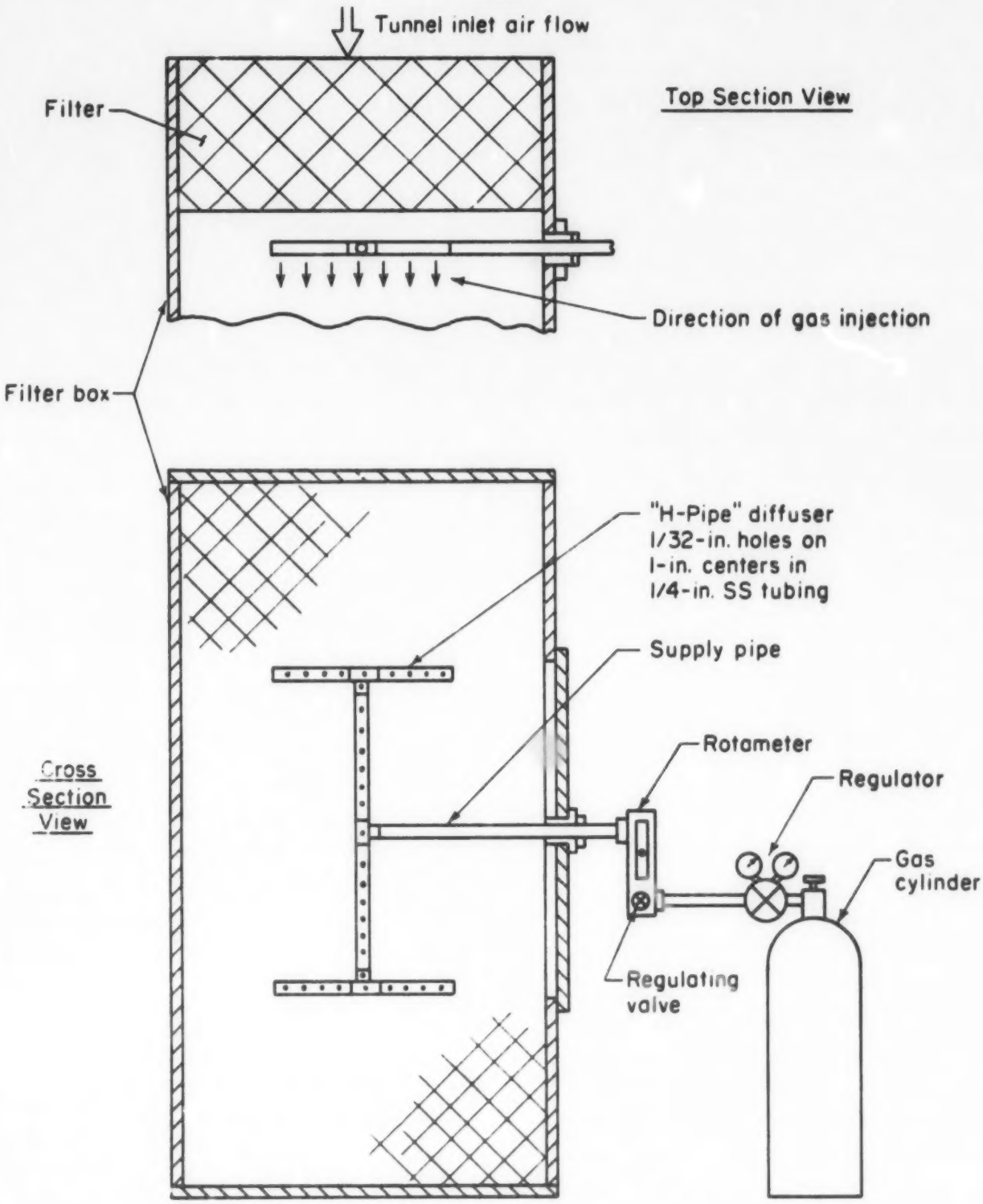


FIGURE A-13. GASEOUS CONTAMINANT INJECTION SYSTEM

with exhaust and dilution air. The H-shaped distributor manifold is installed immediately downstream of the filters in the dilution tunnel filter box, and has 1/32-inch-diameter holes drilled in the downstream side. These holes provide a fairly uniform initial distribution of the contaminant gas in the dilution air stream before it passes through the tunnel orifice, where it is mixed with exhaust.

The injection rate of ammonia was measured by bubbling the gas through a glass tube containing ammonium hydroxide. The flow rate was determined by counting the bubble rate and estimating the bubble diameter when operating with ammonia. The same conditions were duplicated with air, using a calibrated rotameter in the supply line to measure the quantitative gas flow. Becasue of the corrosive properties of ammonia, a rotameter could not be used in direct contact with ammonia for the flow measurement.

Solid Contaminant Injection System

Figure A-14 is a sketch of the dust entrainment apparatus which was used in some tests to add dust as a solid contaminant to the tunnel air. The apparatus consists of a motor driven disc containing four V-shaped grooves. Scraper vanes fill the grooves and level them. The filled grooves then pass under an aspirator which picks up the dust and dispenses it. The feed rate was controlled by the disc speed. The resulting aerosol is fed into the exhaust pipe immediately downstream of the exhaust-gas diverter valve. Dust injected at this point is quickly entrained and mixed with the exhaust gas and the mixture is diluted at the tunnel orifice plate.

Dust Contaminant

The dust contaminant was Fine Arizona Road Dust which was screened before use to remove all particles larger than 3.3 micrometers Stokes diameter. Figure A-15 is a Rosin-Rammler plot of the particle size distribution of the sample of dust as received before the larger sizes were removed and discarded.

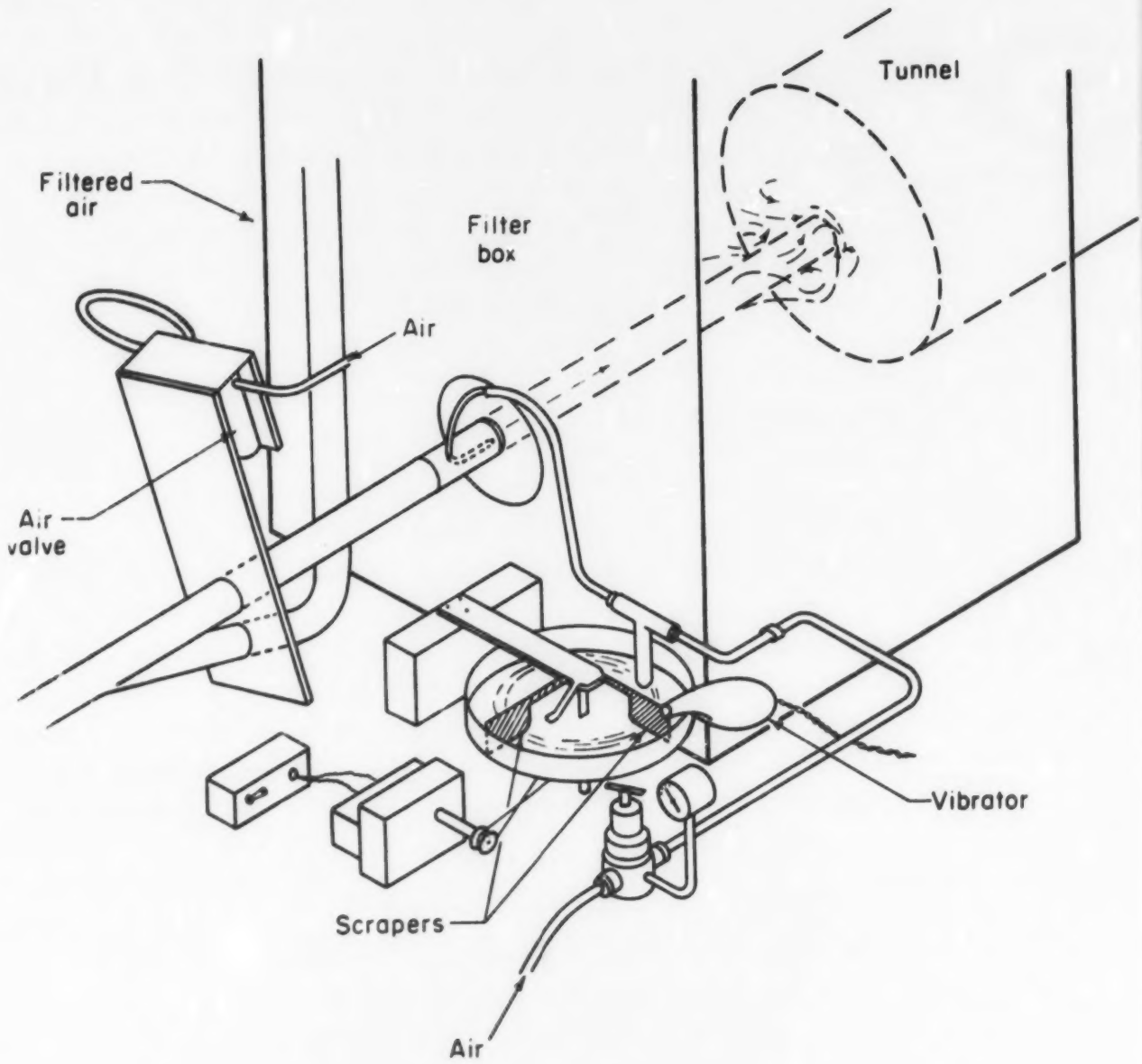


FIGURE A-14. SCHEMATIC OF DUST FEEDER

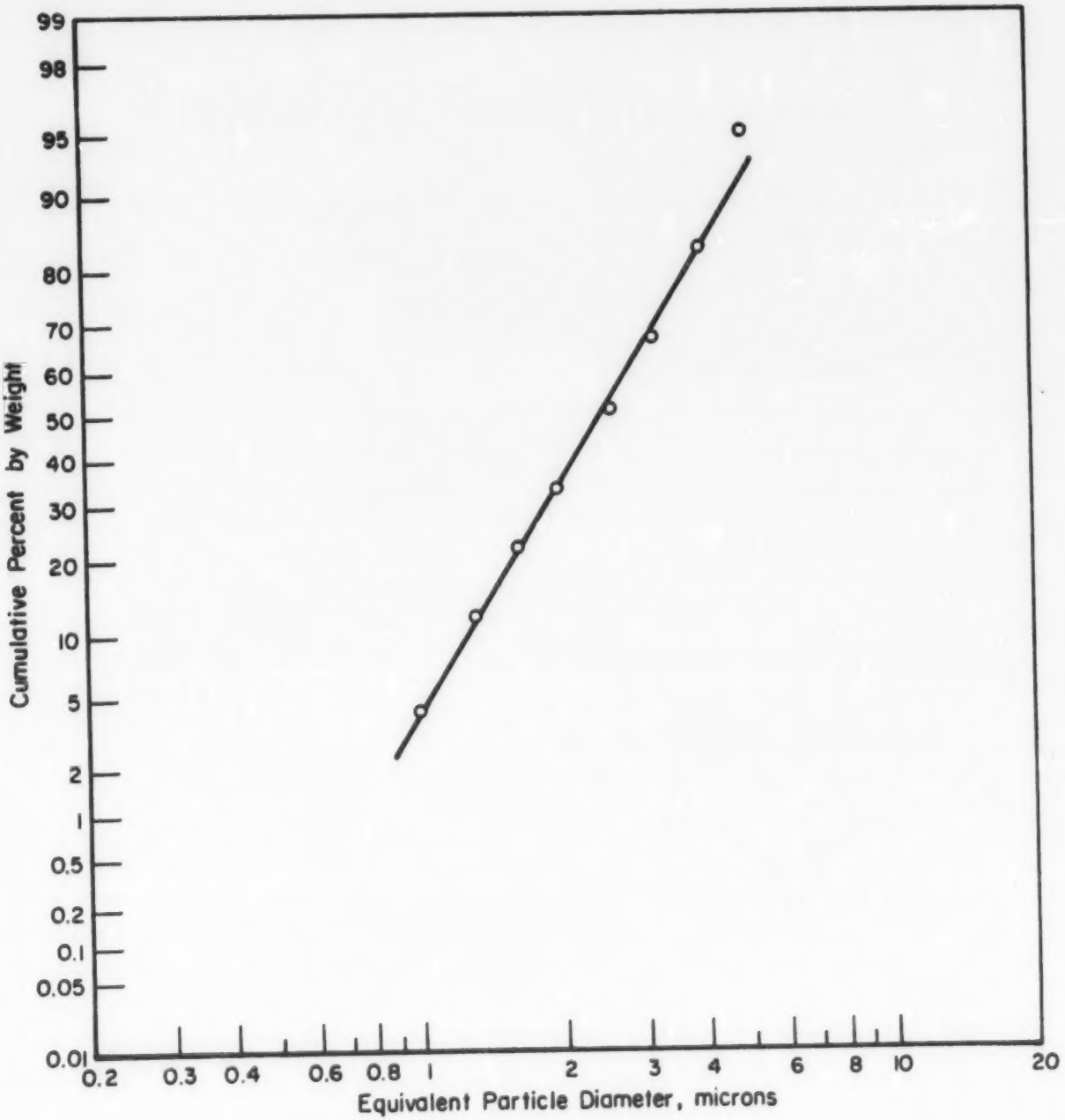


FIGURE A-15. PARTICLE SIZE DISTRIBUTION OF CLASSIFIED ARIZONA ROAD DUST

Chemical composition of the classified dust was determined by optical emission spectrometry, as shown in Table A-5.

TABLE A-5. CHEMICAL COMPOSITION OF FINE ARIZONA DUST

Element	Percent	Element	Percent
Silicon	15-30	Chromium	0.01
Aluminum	5-10	Calcium	2-4
Magnesium	0.7	Vanadium	0.01
Iron	3.0	Copper	0.1
Manganese	0.05	Sodium	1-2
Barium	0.05	Titanium	0.3

Residence Chamber

Chamber Configuration

The residence chamber (Figure 1, page 3) is a rectangular 6-mil black polyethylene bag approximately 9 ft x 12 ft x 20 ft with a filled volume of about 2160 cu ft.

Figure A-16 is a layout of the residence chamber showing sample probes, the sample pipe, and the purge circulation system. Diluted exhaust gases from the dilution tunnel enter the residence chamber through a 2-inch ID PVC plastic pipe which is located approximately 6 ft from one end of the chamber and 4 ft down from the top. The sample pipe projects horizontally into the chamber for a total length inside the chamber of about 5 ft and is curved slightly so that the sample flow is towards one upper corner of the chamber. In the final design, the sample pipe has a tapered discharge nozzle to promote mixing with dimensions as shown in Figure A-17. This design was selected after three series of exploratory measurements with other configurations and locations, described in following sections.

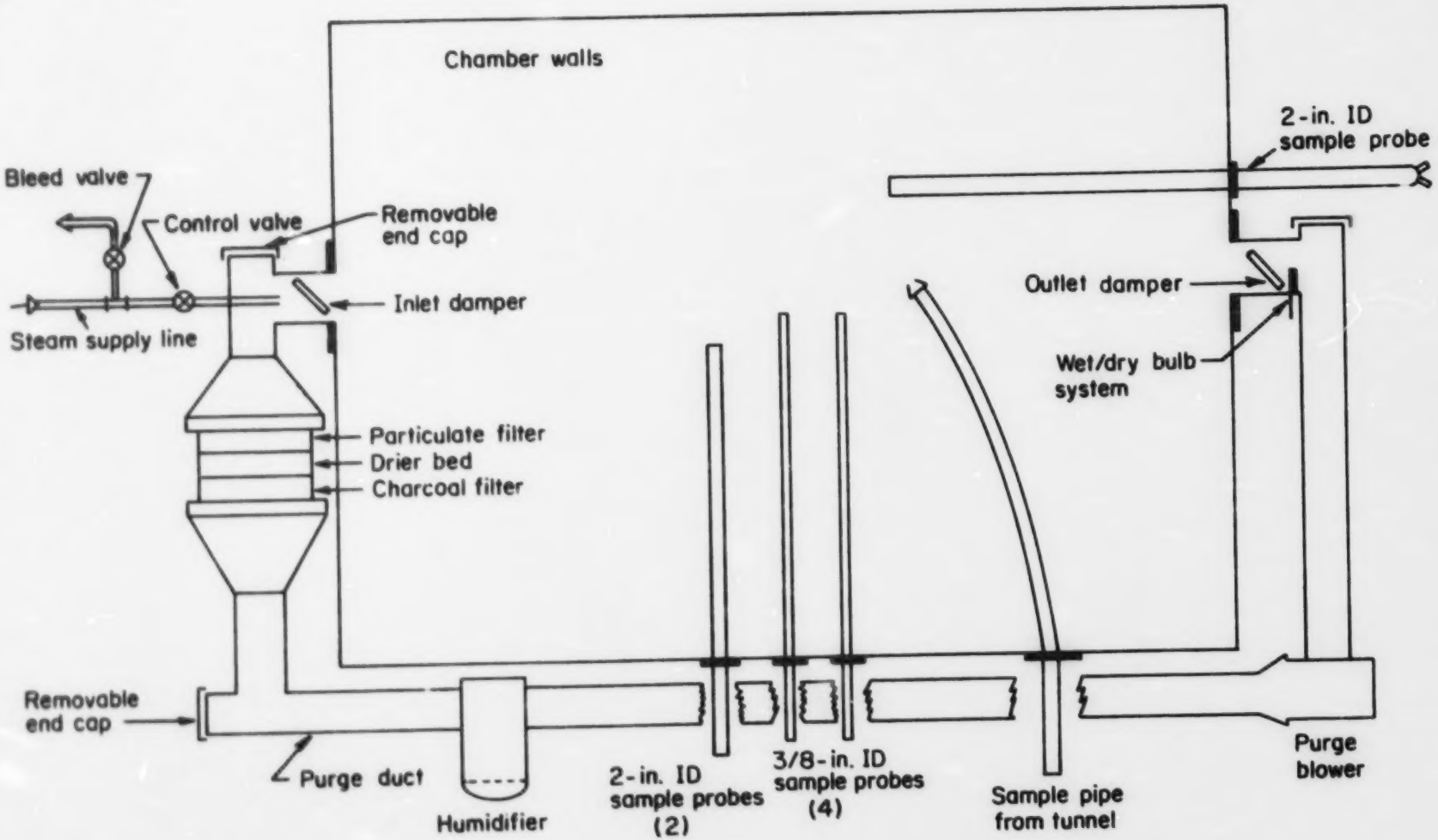
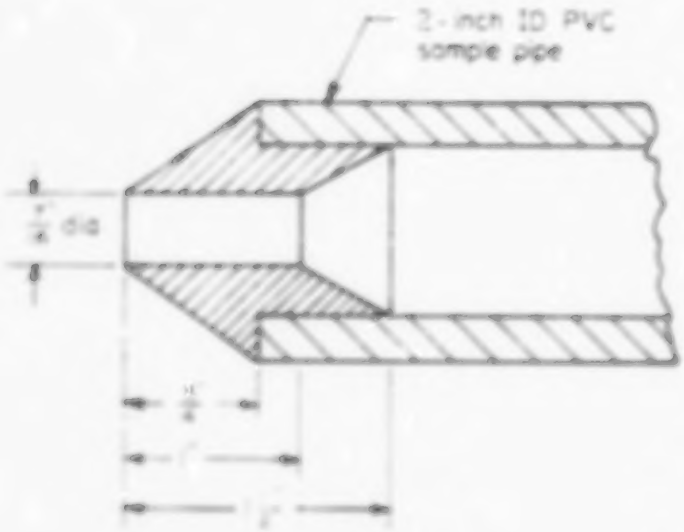


FIGURE A-16. LAYOUT OF RESIDENCE CHAMBER AND PURGE-CIRCULATION SYSTEM


2-inch ID PVC
sample pipe
d/4 dia
d/4
d
1 1/2 d

Chamber samples for gas analysis are withdrawn from the center of the chamber through 3/8-inch-ID stainless steel probes. Samples for particulate and light scattering analysis are withdrawn through two 2-inch-ID PVC sample probes with intakes near the center of the chamber.

Dilution Ratio Experiments

The dilution tunnel when operated at a total flow rate of 905 cfm dilutes the auto exhaust by an average ratio of 30 to 1 at 72 F and 1 atm. To achieve an overall dilution ratio of 300 to 1 in the residence chamber, a tunnel-to-chamber dilution of 10 to 1 is required. Thus, the tunnel sample-point pressure, and the sample-pipe and residence chamber design were selected to achieve this 10 to 1 dilution and to achieve fast and complete mixing in the chamber.

The 2-inch diameter of the tunnel-to-chamber sample pipe was selected to achieve approximately isokinetic sampling from the tunnel. However, the flow through this pipe at 1-inch H_2O differential pressure was considerably greater than required for the 10 to 1 dilution. Consequently, flow was restricted to the desired rate of about 9 cfm with a discharge nozzle at the outlet end.

In the actual test runs, the sampling rate averaged approximately 10 cfm. With an average tunnel flow rate of 905 cfm for the test runs, the isokinetic sample flow rate would be 7.5 cfm for the 2.1-inch-diameter probe opening. Thus, the actual sample flow was about 33 percent greater than true isokinetic flow.

Table A-5 summarizes the results of the first series of nine preliminary dilution-ratio experiments, Runs 9-3 to 9-11, at a tunnel flow of about 1100 cfm. Two locations for flow restriction were compared, one at the discharge end of the pipe inside the chamber and the other in the pipe immediately downstream from the sample-flow control valve. This configuration was a simple orifice-venturi shape with a straight tube between straight-sided conical converging and diverging sections.

These three runs performed before all of the instrumentation was available and operational, hence, only HC and CO measurements were made in the tunnel and chamber to determine dilution ratio. The dilution ratios

TABLE A-6. SUMMARY OF INITIAL TUNNEL-TO-CHAMBER DILUTION RATIO EXPERIMENTS

White Unleaded Car
RE-1418 Fuel
Sample Point Pressure 1 inch H_2O
Tunnel Air Flow, 1100 scfm

Run	Tunnel-to-Chamber Dilution Ratio[a]			Description of Sample-Pipe Restriction
	From HC	From CO	Average[b]	
9-5	4.8	11.9	4.8	Open pipe
9-6	6.5	70.0	6.5	Open pipe
9-7	6.2	5.8	6.0	Open pipe
9-8	12.0	14.8	13.9	3/8-inch nozzle at pipe end
9-12	15.3	13.4	14.4	3/8-inch venturi above valve
9-13	11.0	11.0	11.0	1/2-inch venturi above valve with 1" nozzle at pipe end
9-15	11.0	14.0	12.5	"
9-18	15.2	7.4	15.2	"
9-20	10.0	17.2	10.0	"

(a) Computed from HC and CO measurements in tunnel bag and in residence chamber before and after run.

(b) Average value taken as value computed from HC data only when HC and CO data were not in ± 10 percent agreement, because of intermittent malfunctions of CO meter.

computed from both HC and CO measurements are presented. However, the HC data are considered more reliable wherever the two numbers do not agree well, because of intermittent malfunctions of the CO meter.

One configuration, which gave adequate control of flow, had the 1/2-inch primary restriction located downstream of the sliding plate valve used to cut-off sample flow (Figure A-10, page A-22), plus another 1-inch-diameter nozzle at the tube end in the chamber. The last four tests, 9-13 through 9-20, were reproducibility tests run with this restriction configuration. It was concluded that flow control was acceptable, but mixing in the chamber was too slow.

Chamber Mixing Experiments

Beginning with Test 9-15, Table A-6, dilution ratios and mixing in the chamber were investigated at the same time. It was found initially that mixing was completed 15 to 30 minutes after the end of the auto-exhaust-generation run. Particle concentrations were then similar in various regions in the chamber.

In a second series of tests a more detailed evaluation of chamber mixing was made with propane tracer, using short sample probes temporarily installed in four corners of the chamber. These probes projected 1 inch into the chamber and were each located within about 6 inches of the corner so that they would be sampling from extreme regions of the chamber. The regular sample probes in the center of the chamber were also used. The mixing-study probe locations (listed in the sampling sequence generally used in the tests) were: side center near chamber middle, side center near chamber wall, top southeast corner near wall, bottom southwest corner near wall, top northwest corner near wall, bottom northeast corner near wall. A full sampling sequence required approximately 12 minutes. This allowed about 2 minutes at each position to stabilize the reading and to note short-term changes of the record.

A total of 11 experimental runs were conducted in the propane-mixing study. Propane (LPG from a cradle-type tank) was introduced into the tunnel dilution tube with the tunnel air flow at approximately 600 scfm and with a sample-point pressure of 1 cm H$_2$O. The rate of propane injection was adjusted to yield a concentration around 800 to 1000 ppmC in

the tunnel. When stabilized conditions were obtained in the tunnel, the residence-chamber sample valve was opened for a period of 23 minutes, the standard LA-4 cycle running time. Immediately following the end of this sampling period the concentrations of HC in the residence chamber at the various sample-probe positions were measured in the predetermined sequence. The sequence was repeated several times over periods up to almost an hour after the end of the sampling period.

With the 1-inch-diameter nozzle opening at the end of the sample pipe in the chamber used in the first series, the velocity of the gas leaving the pipe was about 28 ft per second. This was insufficient to promote rapid mixing into corners of the chamber.

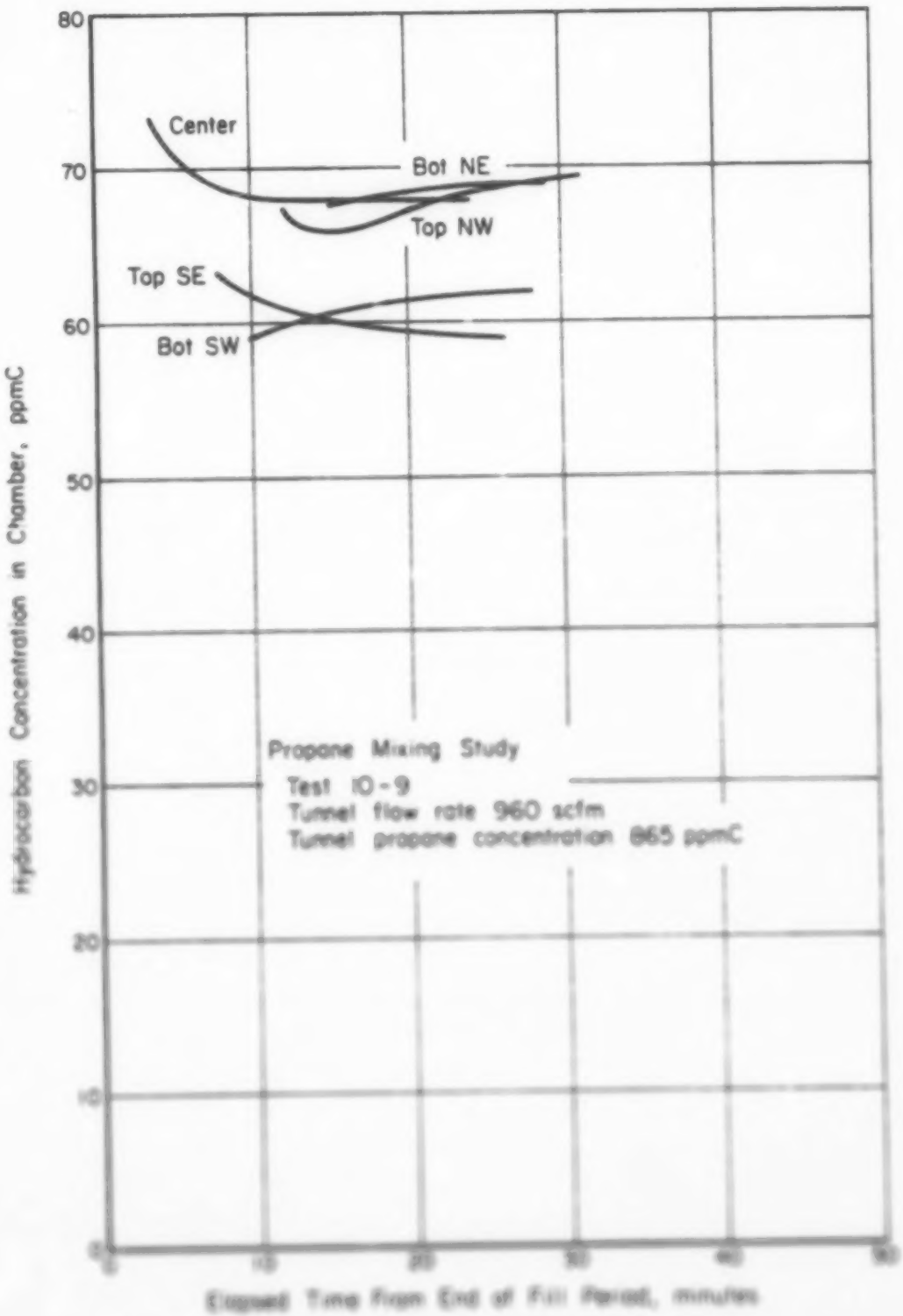
Experiments in the third series were then conducted with one sample-pipe flow restriction located only at the pipe end. Mixing was substantially improved, and nozzle dimensions of 7/16-inch diameter by 1 inch long were found to yield the desired final dilution ratio. With this nozzle (Figure A-17, page A-34) the velocity of the gas entering the chamber at 9 cfm flow rate was about 145 ft per second. A uniform mixture in the residence chamber was obtained 12 minutes after injection was completed at the end of the test run, at which time all HC concentrations agreed within 10 percent. Figure A-18 shows the time variation of the HC concentrations in the residence chamber from the various sampling probes after the simulated auto-exhaust run with propane, with the final modification of the mixing nozzle in place.

Chamber Humidification

High residence chamber humidity was initially achieved in Runs 10-13 to 12-4 (Table A-4, page A-19) by injecting steam directly into the chamber with the purge-circulation system in operation.

This method worked quite well for bringing the chamber up to 70 percent relative humidity in a short time, but it produced an unacceptable increase of the background particle level in the chamber.

Other methods were tried and the final technique selected combined the use of steam to raise the humidity in the whole laboratory, the injection of some steam directly into the purge system makeup-air inlet (Figure A-11, page A-33) and the use of a wick-type humidifier in the purge system line as shown in Figure A-10 (also Figure A-11, page A-33). The


80
70
60
50
40
30
20
10
0
Center
Bot NE
Top NW
Top SE
Bot SW
Propane Mixing Study
Test 10-9
Tunnel flow rate 960 scfm
Tunnel propane concentration 865 ppmC
Hydrocarbon Concentration in Chamber, ppmC
Elapsed Time From End of Fill Period, minutes

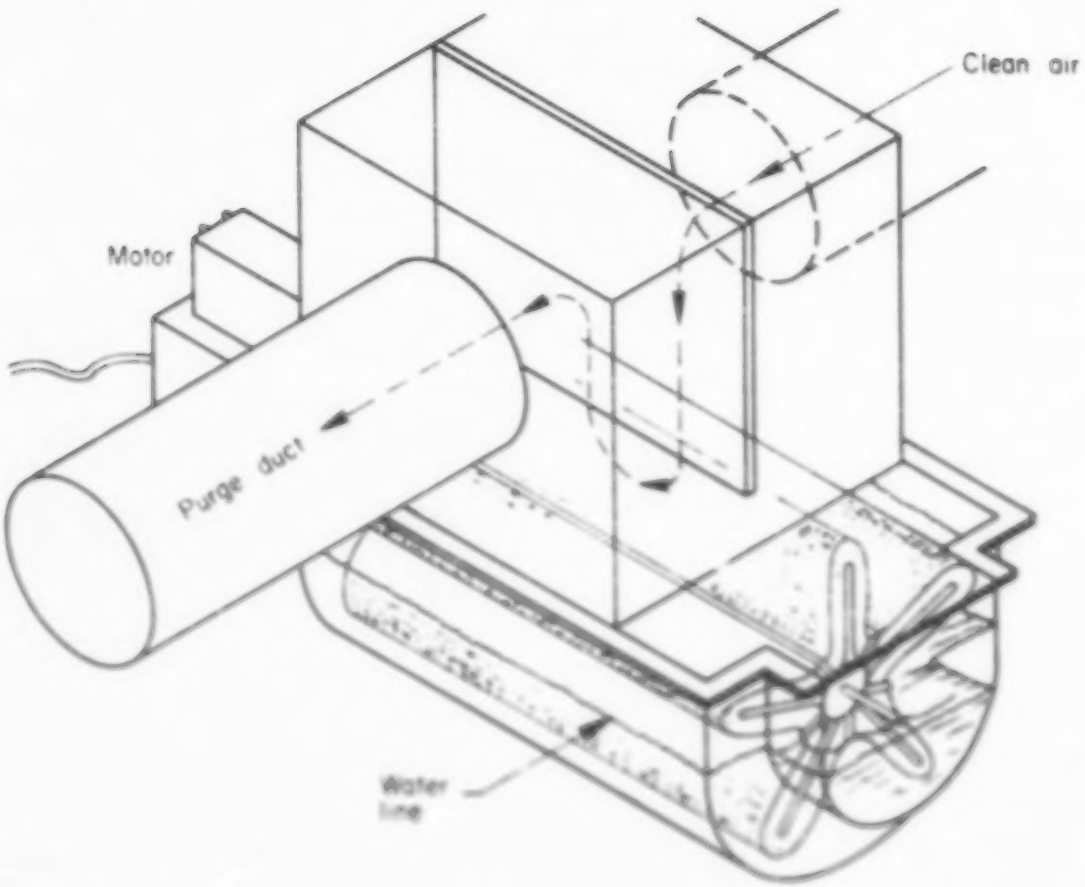


FIGURE A-19. SCHEMATIC OF WICK-TYPE HUMIDIFIER IN HEATSHOCK CHAMBER PURGE DUCT

humidified air passes through the filters before entering the chamber. This technique requires a longer period of time but does not affect the background particle concentration in the chamber.

Dilution Ratio Definition and Method of Calculation

The dilution tunnel dilution ratio is the total tunnel flow divided by the exhaust flow. The residence chamber dilution ratio is the total residence-chamber volume (after sample addition) divided by the volume of diluted exhaust gas added to the residence chamber.

Dilution tunnel dilution ratio is computed directly from measured tunnel flow and exhaust flow. Residence chamber dilution ratio is computed indirectly from measurements of CO and HC concentrations in the chamber, before and after sample addition, and in the tunnel bag sample.

The development of residence-chamber dilution-ratio equations follows.

Symbol Definitions

Let: Q_a = residence chamber volume before sample addition

Q_s = volume of diluted exhaust gas added to residence chamber during driving cycle

Q_f = final volume of residence chamber after sample addition

C_a = HC or CO concentration in residence chamber before sample addition

C_s = HC or CO concentration in diluted exhaust gas

C_f = HC or CO concentration in residence chamber after sample addition.

Equations

$$D.R.\ (\text{dilution ratio}) = \frac{Q_f}{Q_s} \quad \ldots \quad (1)$$

$$Q_a + Q_s = Q_f \ (\text{summation of volumes}) \quad \ldots \quad (2)$$

$$Q_a C_a + Q_s C_s = Q_f C_f \ (\text{summation of emission mass}) \quad \ldots \quad (3)$$

Solve equations (1), (2), and (3) simultaneously:

$$\frac{Q_a C_a}{Q_s C_a} + \frac{Q_s C_s}{Q_s C_a} = \frac{Q_t C_t}{Q_s C_a}$$

$$\frac{Q_t - Q_s}{Q_s} + \frac{C_s}{C_a} = (D.R.) \frac{C_t}{C_a}$$

$$(D.R.) - 1 - (D.R.) \frac{C_t}{C_a} = - \frac{C_s}{C_a}$$

$$D.R. = \frac{C_s - C_a}{C_t - C_a} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

Instrumentation

Gas Analysis

Direct reading and recording instruments were used for analyses of gases from the tailpipe, the dilution tunnel, the residence chamber, the filtered dilution air, and composite bag samples from the dilution tunnel. In general, each instrument zero was set with a zero gas and the span with one or more span gases covering the range of expected concentrations. The span and zero were checked and adjusted before and after each run. Manufacturers' guaranteed values for gas composition were accepted for standard gases to set zero and span at the reported concentration of the span gas, and the instrument manufacturers' calibration curves were relied on for interpolation and extrapolation. There was no absolute standardization by analysis of the standard gases. On some occasions, zero gas and two standard gases were used to construct a revised curve through the origin and these two additional points. Table A-7 shows the record of instruments used during the year while developing the capability to obtain reliable emissions of exhaust gas composition. Some instrumental difficulties were identified and corrected as soon as they were recognized. Specific details on calibrations and substitutions are described in tabulated comments discussing the individual gases.

TABLE A-7. GAS ANALYSIS INSTRUMENTS

Samples				Instruments			
					Standard Gases		
Veh	Location	Time	Approx. Conc.,[a]	Description	Concentrations	Use Period	Comments on Techniques and Instruments
	Tailpipe	Continuous record incl. A/F ratio modes	1-5%	Olson-Horiba IR	0, 4.9%	12/6-5/22	Range 0-10%
69	Tunnel	Cycle record	2-400 ppm	Beckman NDIR	0, 152 ppm 0, 152, 220 0, 152,1075	12/6-4/25 4/26 5/9-5/22	Instrument malfunction 4/11-4/20; corrected 4/25. Emissions above 1972 limit 4/11-4/26; adjusted to below limit, 5/9→. Bag samples from tunnel 4/25, 4/26, instead of continuous recorded analysis.
	Chamber	Continuous 11/29-1/23 and 0, 30' 4/11 →	Low	Same			
	Background	Bag sample	Low	Same			
	Tailpipe	A/F ratio modes	1000 - 2000 ppm	Beckman FID	0, 76.3 ppm	12/6-5/22	Tailpipe sampled for HC following cycle during idle, 35 mph, 50 mph modes. Span calibration before and after cycle and after 50 mph mode.
	Tunnel	Cycle record	50 - 100 ppm	Same			Measurement used to detect abnormal conditions.
60	Chamber[a,b]	0, 30'	Low	Same			Ditto
	Tailbag and	Bag sample	Low	Same			"

[a] Chamber sample at zero time gives background concentration in chamber; at 30 minutes gives concentration after dilution and mixing in the chamber.

TABLE A-1 (CONTINUED)

Samples				Instruments			
					Standard Gases		
Lab.	Location	Time	Approx. Conc., ppm	Description	Concentrations	Use Period	Comments on Techniques and Instruments
	Tailpipe	A/F ratio measurement		Beckman 715	Air, 21%	11/29-1/23	First and second instruments gave unsatisfactory and unreliable measurements. Identical models.
				Beckman 715	Ditto	Ditto	
R_2				Beckman 715	0.54,2.2%	4/11-4/26	Third instrument gave acceptable results with improved techniques, using long sampling time for slow response.
				Beckman GM-11	Ditto	5/9-5/22	Excellent results: Stable reading with fast response.
	Tunnel	Bag sample	1-20 ppm	Beckman NDIR 0-250 ppm range	140 ppm	11/29-1/12	Doubtful results
	Chamber	O_3 10'			140,19 ppm	1/12-1/23	Revised calibration curve to fit two gases. Improved technique with drastic dehydration in better cold trap. Overhauled instrument. Good results obtained with changes.
R3	Dilution air	Bag sample			Ditto	4/11-5/22	Reliable results.

TABLE A-7. (CONTINUED)

Gas	Samples: Location	Samples: Type	Samples: Approx. Conc.[a]	Instruments: Description	Instruments: Standard Gases: Concentrations	Instruments: Standard Gases: Use Period	Instruments: Comments on Techniques and Instruments
CO_2	Tailpipe	Bag samples		Beckman NDIR	9.94% 12.4%	11/29-4/20 4/25-5/22	Instrument recorded sample from tailpipe 11/29-4/20 and 5/18-5/21. Bag samples carried to instrument 4/25-5/17. Two span gases disagreed. Difference represents 3% of measurement.
	Tailpipe	Direct reading 0, 25, 50 mph for A/F ratio					
	Tunnel	Cycle record		LIRA IR 0-1%	1100 ppm 7240	11/29-1/23 4/11-5/22	1100 ppm gas used routinely; 7240 ppm occasionally to check calibration curve. Curve corrected to conform to two concentrations of span gases.
	Chamber	0, 50°		Ditto	Ditto	Ditto	
	Dilution air	Bag sample		"	"	"	

Speed Controller

A speed controller was used to drive the test car automatically through the LA-4 driving schedule after it was manually started and shifted into gear. During exploratory tests and choke schedule development, cars were driven by a Research Incorporated (RI) controller, programmed by a punched-paper tape (Table A-4, page A-19). Problems were encountered with faulty control by this instrument in a few tests and it was taken out of service for repair. While the system was being serviced, a second speed controller, manufactured by Dynamic Precision Controls (DPC) and using a magnetic tape program input, was used for Runs 12-1 to 12-22. The RI punched-tape system was put back in service and used for Runs 1-3 to 1-15.

The DPC magnetic tape speed controller system drives the car through a more precise cycle than the RI punched tape speed controller, because the punched tape tends to smooth out the minor speed fluctuations. Therefore, a new DPC magnetic tape controller was obtained for all subsequent tests.

Minnesota Aerosol Analyzing System[1]

A group of instruments known as The Minnesota Aerosol Analyzing System (MAAS) was available on loan for some of the runs (Table A-4, page A-19) and was used whenever available to characterize the size distribution of automotive exhaust particles in suspension in samples removed from the dilution chamber.

The MAAS consists of three aerosol particle counters in parallel operation, which in combination measure the aerosol size distribution from 0.0032 to 10.0-μm diameter. The instruments consist of a modified Royco Model 225 optical counter, a condensation nuclei counter (CNC), and a electric aerosol analyzer (EAA). The output of the optical counter is fed into a Nuclear Data ND 415 computer, and the outputs of CNC and EAA are fed into a Hewlett Packard Data Acquisition System (HP).

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[1] Courtesy of Professors Whitby of the University of Minnesota and Dr. William Wilson, Jr., of National Environmental Research Center, CPD.

(1) K. T. Whitby, B. Y. H. Liu, R. B. Husar, and N. K. Barsic, J. Colloid and Interface Science, Vol. 39 No. 1, pp 136-164 (April, 1972)

The size range of the multiwire Royco Model 220 sensor is from 0.503 to 10.0 um, and this range is classified into 512 channels under control of the SD 812 computer.

The condensation nuclei counter is a standard Environment-One counter operated at an under-pressure expansion of 5 inches of Hg vacuum.

The Whitby Aerosol Analyzer is an improved ion mobility analyzer manufactured by Thermo Systems, Inc. The instrument has feedback-controlled high-voltage power supplies which permit automatic operation in conjunction with the DAS. It covers the size range between 0.0032 and 0.502 um and the minimum scan time is 2.0 minutes.

Studies of Filtration and Weighing Procedure

The mass concentration of exhaust particles was determined by measuring the net weight gain of an absolute filter for filtration of a measured volume of diluted auto exhaust. A procedure was developed to check the validity of the weight gains measured. Operations made a part of this procedure are described in following sections.

Thermal Decay in Controlled Atmosphere Balance Room

A new Mettler Model H5 microbalance with a platinum sensitivity of 1 ug was set up and used exclusively on this project in an enclosed room with controlled constant humidity and temperature. The microbalance was also used temporarily in a controlled humidity glove box, and in two other ambient-atmosphere rooms, but some results that were initially below the sensitivity limitation were found.

Repeatability of Weighings with the Microbalance

Early data generally showed that a reproducibility of two times of sigma, a check on short drift, and a final 5 minutes for no weight. The zero weight check was taken one hr to check on the operation of the balance and on the constancy of the ambient particulate the weighing. In

TABLE A-8. REPETITIVE WEIGHINGS OF BLANK FILTERS AND OTHER MATERIALS

Oct. 23 1972 Time	Weights, g				Temperature, F	Relative Humidity, %
	47-mm Glass Filter MSA J7864	Stainless Steel Disk	142-mm Metricel Filter DM450	Type M 500 mg Platinum Wt.		
8:00	0.105173	0.213274	0.574450	0.499996	72.3	41.0
10:00	0.105181	0.213274	0.574545	0.499996	73.5	46.0
12:00	0.105170	0.213265	0.574478	0.499995	74.0	48.8
2:00	0.105165	0.213263	0.574509	0.499994	75.0	46.5
4:00	0.105173	0.213272	0.574413	0.499995	73.0	28.5

this room the maximum humidity was controlled below 50 percent RH, but there was no control of minimum relative humidity. The temperature was controlled between 72.3 and 75.0 F in the weighing area.

The apparent weight gains and losses of the filters in Table A-8 did not correlate consistently with increases and decreases in humidity. Therefore, the variations in these weights were suspected to be attributable to other causes, such as changes in electrostatic charge. A small polonium source had been used routinely in the balance during these weighings to dissipate static charges, but the observed variations, if caused by electrostatic charge, meant that the dissipator was undersized.

Two new and larger polonium sources were then used to initiate another series of experimental weighings (data not given). Prior to each weighing, both sides of each filter were exposed at a distance of one inch from these polonium sources. After this pretreatment, uniform weights of ± 4 μg were obtained until there was a change in humidity. When the humidity remained within ± 1.0 percent RH, the weight of a 47-mm Metricel filter is repeatable within about ± 15 μg and that of a 142-mm Metricel filter is repeatable within about ± 150 μg. The larger size has approximately ten times the surface area subject to adsorption and desorption of water vapor.

Filter Media

Two types of polymeric membrane filters were selected for use in the determination of particulate mass by weighing. Metricel DM 450 membrane filter (Gelman Instrument Company, Ann Arbor, MI, Part No. 64519) is a copolymer of polyvinyl chloride and acrylonitrile, 0.45-μm pore size. The filter diameter was 142 mm. The filter was used in a filter holder with an active filtration area of 125 cm^2. Flow rate, calibrated for each batch, was about 7 cfm for one filter in the holder and about 4.3 cfm for two in series, with a pressure drop of about 10 cm Hg across the filter(s). Face velocity at 4.3 cfm was 16.3 cm/s.

Millipore MF AAWP 047 00 membrane filter (Millipore Filter Corporation, Bedford, MA) is a mixed cellulose ester, reportedly propionate-butyrate, 0.8 μm pore size. Filter diameter was 47 mm, and active

filtration area was 9.6 cm^2. Flow rate calibrated for each batch was about 1.0 cfm for one filter and 0.7 cfm for two in series in the holder, with a pressure drop of about 10 cm Hg across the filter(s). Face velocity at 0.7 cfm was 34.4 cm/s.

The membrane filters were chosen because they were expected to be low in reactivity toward acidic constituents (e.g., SO_2) in the exhaust, and resistant to abrasive losses during insertion in and removal from the filter holders. Agreement in results from simultaneous parallel samples taken with both types indicated probably negligible effects on weight gains because of filter holder configuration, face velocity of the filtered stream, and chemical composition of the filter medium.

Filter-holder flow rate was controlled by an orifice downstream of the filter. Orifices for each filter holder were calibrated with the proper filters in place, using a dry gas meter, and at the same manifold vacuum as was used during the actual sampling runs. The calibrations were repeated several times during the program to determine that no substantial changes in flow rate were taking place.

The SO_2 content of the automobile exhaust was determined, in order to estimate whether the potential weight change of a reactive filter would be significant if the sulfur in the fuel (0.036 wt %) were converted to SO_2 followed by reaction with the filter. It was found that the SO_2 in the exhaust diluted in the tunnel ($\sim$30:1) contained approximately 0.2 ppm SO_2. A 22-liter sample contained by analysis 10.5 micrograms of SO_2. In tests that use a 4.0 cubic meter sample volume, SO_2 could account for 2,000 micrograms weight increase of the filter if all the SO_2 reacted with the filter. This is about the same as the weight of particles collected from unleaded fuel during one LA-4 cycle so that the effects of reactions between filter and any substantial part of the SO_2 would invalidate the particle weight data.

On the other hand, these neutral filter media change weight with humidity changes and by adsorption of exhaust constituents. This disadvantage was compensated by using a second filter disc as backup in each filter holder, and by applying the change in weight of the backup filter as a correction to the measured weight change of the primary filter.

Pattern of Sampling for Particulate Matter

Four simultaneous samples were filtered for determination of particulate mass in almost all experimental tests: two were 142-mm Metricel filters in stainless steel holders with conical approach sections, and two were 47-mm Millipore filters in holders of similar configuration.

Two filter discs were placed in each holder, with the primary filter for particle collection, and the backup filter as a weight-change control. The weight change in each filter following exposure was determined by separate weighings.

The efficiency of these filter media is so high that no solid particulate matter can penetrate to a backup filter in the same holder. Therefore, the algebraic difference between the weight changes of the primary and the backup filter after both have been exposed in series to the same sample stream is a measure of the weight of solid particulate collected on the primary filter. It is assumed that the gas stream is not significantly changed in composition by passage through the first filter and that weight changes from adsorption or desorption of its constituents on the filter structure are the same in each of the two filters.

Experimental Results--Supplementary Data

Test Conditions

Table A-9 summarizes pertinent laboratory conditions and Table A-10 gives calculated air-fuel ratios for the modified and standard LA-4 cycle test runs. All the runs are included where essentially complete data were acquired. Problems were encountered on Runs 4-10 and 4-18, which are noted on the tables. Any significant deviations in the test conditions from target or normal values are described in footnotes of the tables.

The A/F ratios of Table A-10 were determined from CO, CO_2, O_2, and HC measurements made in the tailpipe at steady-state conditions of 0, 35, and 50 mph immediately following each test run. Each entry is the mean of three values determined from CO-O_2, CO-CO_2, and O_2-CO_2, using the Eltinge charts. CO_2 and O_2 were corrected for HC. A fuel H/C ratio of 1.90 was assumed.

TABLE A-9. LABORATORY AND OPERATING DATA FOR MODIFIED AND STANDARD LA-4 CYCLE RUNS

Run No.	Run-in Mileage[a]	Soak Time, hours	Avg. Soak Temperature, °F	Laboratory Temperature, °F	Laboratory Humidity, gr/lb dry air	Chamber Humidity[b], percent	Run Length[c], min
Unleaded Fuel Tests							
4-10[d]	42	19.4	69	71	37	34[g]	23.41
4-11	101	16.5	68	70	29	28	23.25
4-12	120	17.0	72	69.5	35	33[g]	23.37
4-13	139	16.3	70	68.5	31	30	23.28
4-16	109	17.5	70	74	48	37[g]	23.26
4-17[f]	117	14.2[h]	70	70.5	48	41[g]	22.75
Leaded Fuel Tests							
4-18[e]	60	13.6[h]	70	73	75	50[g]	25.13
4-20	126	18.1	70	77.5	68	35[g]	23.53
4-25	122	14.7[h]	70	71	37	30	23.37
4-26	111	17.0	70	73	44	26	23.35
Unleaded Fuel Tests							
5-15	116	17.1	70	70	37	30	23.37
5-16	122	16.7	70	70	40	30	23.40
5-17	120	17.1	70	69	35	29	23.40
5-18[f]	124	16.8	70	71	39	27	22.83
5-19[f]	121	15.7[h]	70	71.5	46	27	22.78
Leaded Fuel Tests							
5-9	121	16.7	70	77	59	31	23.40
5-10	114	17.2	70	72	67	42[f]	23.42
5-21	108	15.9[h]	70	71	51	29	23.40
5-22	118	16.7	70	75	62	34	23.40

(a) Generally includes about 100 miles on the NVHA Durability Driving Schedule and two consecutive LA-4 cycles.

(b) As measured by wet and dry bulb thermometers just before start of the test run.

(c) Time-sequence clock on to clock off 5 seconds after vehicle stops on last mode, unless otherwise noted, this time period also represents the interval the exhaust-gas diverter valve opens the tailpipe to the tunnel and the interval of tunnel-bag sampling.

(d) The tunnel-bag sampling was inadvertently continued for about 40 seconds after the clock was stopped, sampling dilution air only. The mass gaseous emissions have been corrected for a 3 percent dilution; the run-in mileage for this test was also low.

(e) The engine killed when put in gear, was restarted and test continued to completion with about 104 seconds additional time before first mode started. The run-in mileage for this test was also low.

(f) Tests 4-17, 5-18, and 5-19 are standard FTP-cycle tests.

(g) The chamber humidity on Tests 4-10, 4-12, 4-16, 4-17, 4-18, 4-20, and 5-10 was above target of 30 percent.

(h) The soak time on Tests 4-17, 4-18, 4-25, 5-19, and 5-21 was less than the target of 16 hours, but all were greater than the FTP requirement of 12 hours.

TABLE A-10. AIR-FUEL RATIOS DETERMINED FROM STEADY-STATE EXHAUST-GAS ANALYSES AFTER EACH RUN

Run No.	Air-Fuel Ratio[a]		
	Idle	35 mph	50 mph
	Unleaded Fuel Tests		
4-10[b]	14.90	15.23	--
4-11	14.29	15.46	15.15
4-12	14.23	15.39	15.02
4-13	14.22	15.43	15.10
4-16	15.01[e]	15.26	15.03
4-17[c]	14.85[e]	15.38	15.16
	Leaded Fuel Tests		
4-18[d]	15.33	15.22	14.90
4-20	14.49	14.91	14.78
4-25[g]	14.21	15.07[f]	14.90[h]
4-26[g]	13.96	15.02[f]	14.82[h]
	Unleaded Fuel Tests		
5-15[g]	15.10[d]	15.60	15.20[h]
5-16[g]	14.97[d]	15.57	15.18[h]
5-17[g]	14.66[d]	15.59	15.17[h]
5-18[c]	14.64[d]	15.59	15.17
5-19[c]	14.61[d]	15.48	15.17
	Leaded Fuel Tests		
5-9[g]	15.65[h]	15.31[h]	15.10[h]
5-10[g]	14.83[h]	14.79[h]	14.60[h]
5-21	14.32	14.85	14.86
5-22	15.24	14.60	14.59

(a) Determined by measurement of concentrations of CO, CO_2, O_2, and HC in tailpipe immediately after test run at steady state modes indicated, and using Eltinge chart for fuel H/C atom ratio of 1.90.

(b) CO_2 values questionable and therefore not used.

(c) Tests 4-17, 5-18, and 5-19 are standard FTP-cycle tests.

(d) CO and O_2 values both high--exhaust system and sampling system checked for leaks, spark plugs and ignition system checked, compression pressures measured.

(e) Oxygen values questionable and therefore not used.

(f) CO_2 values not available on these tests.

(g) The CO_2 instrument was moved to another lab, so idle and 50 mph CO_2 values were obtained by collecting samples in polyethylene bags and transporting to instrument for reading within 1 hour.

(h) A/F number spread from 3 sets of values large compared to other data.

Table A-11 gives the overall dilution ratio in the residence chamber of the samples taken for measurement of mass concentrations. The target for overall dilution ratio was 300. Experimental variations are caused by differences in the amount of filtered air held in the residence chamber by partially collapsing the flexible walls. The tunnel sample was then injected for the final dilution. The variations in ratio shown in Table A-11 are acceptable.

TABLE A-11. DILUTION RATIOS OF DILUTED EXHAUST IN RESIDENCE CHAMBER FOR MODIFIED AND STANDARD LA-4 CYCLE RUNS

Run No.	Overall Dilution Ratio[a]	Run No.	Overall Dilution Ratio[a]
4-10	--	5-15	265
4-11	223	5-16	275
4-12	284	5-17	325
4-13	278	5-18[b]	325
4-16	268	5-19[b]	325
4-17[b]	293		
4-18	278	5-9	268
4-20	262	5-10	297
4-25	271	5-21	332
4-26	252	5-22	

(a) Calculated using average dilution ratio in tunnel of 31.9 and measured dilution ratio from tunnel to chamber using HC values.

(b) Tests 4-17, 5-18, and 5-19 are standard LA-4 cycle tests.